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2-*O*-α-D-GALACTOPYRANOSYL GLYCEROL HEXAACETATE FROM *RUELLIA BRITTONIANA*

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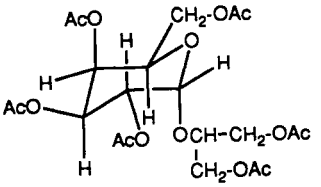
ABSTRACT.—An extract of the whole plant of *Ruellia brittoniana* has afforded the new glycoside 2-*O*-α-D-galactopyranosyl glycerol hexaacetate [**1**]. Its structure and absolute configuration were deduced by spectroscopic methods and X-ray crystallographic analysis.

Ruellia brittoniana E. Leonard (Acanthaceae), native to Mexico, grows as an ornamental undershrub in Pakistan (1). Different species of the genus *Ruellia*, such as *Ruellia prostratus* Nees, *Ruellia suffruticosa* Voigt, and *Ruellia patula* Jacq., have been used to cure gonorrhea, syphilis, and renal infections (2–4). In view of the medicinal properties attributed to *Ruellia* species, we decided to carry out a chemical investigation of *R. brittoniana*. No work on the chemical constituents of this species is reported in the literature. In this paper we report the isolation of the glycoside 2-*O*-α-D-galactopyranosyl glycerol hexaacetate [**1**] from *R. brittoniana*. The structure was determined through spectral and X-ray diffraction analysis.

RESULTS AND DISCUSSION

Compound **1** was crystallized from CH_2Cl_2 as white needles, mp 97°, $[\alpha]_D$ +62° ($CHCl_3$). The fdms displayed a molecular ion peak at *m/z* 506 corresponding to the formula $C_{21}H_{30}O_{14}$.



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The mass spectrum also showed peaks at *m/z* 466 $[M-HOAc]^+$ and 330 [M − glycerol diacetate]$^+$. The uv (MeOH) spectrum showed only end absorption at 205 nm, suggesting no conjugation. The ir ($CHCl_3$) bands at 1720 and 1086 cm^{-1} were indicative of a carbonyl group and ether linkages. Significantly, the ir showed no OH absorption.

The ^{1}H-nmr spectrum ($CDCl_3$) of **1** was particularly informative. The signals for a galactose appeared at δ 5.08 (H-2), 5.33 (anomeric proton), 5.45 (H-4), 4.38 (H-5), 4.10 (H-6α), and 4.14 (H-6β). The signals of glycerol protons appeared at δ 4.22 (H-2′) and 4.00–4.10 (H-1′ and H-3′). The acetyl methyl signals appeared between δ 1.98 and 2.12. The point of attachment of glycerol unit to the galactose moiety was deduced from ^{1}H-nmr, ^{13}C-nmr, COSY, and nOe experiments, and it was found that the C-2′ of glycerol was attached to the C-1 of galactose. The ^{13}C-nmr spectrum of compound **1** showed all 21 carbon signals. The signals at δ 61.64, 63.38, and 63.66 were due to the three methylenic carbons, two of them belonging to the glycerol moiety. Acetyl methyl signals appeared at δ 20.61, 20.64, 20.69, and 20.83. The ^{13}C-nmr assignments were further confirmed by DEPT experiments (5) and are summarized in Table 1.

A suitable crystal of **1** was selected for X-ray diffraction studies. The crystal be-

TABLE 1. ^{1}H- and ^{13}C-nmr Data of 2-*O*-α-D-Galactopyranosyl Glycerol Hexaacetate [**1**].

Position	^{1}H mr	*J* (Hz)	^{13}C nmr
	ppm		ppm
1	5.33, d	3.6	96.02
2	5.08, dd	3.6, 11.0	67.31
3	5.33, dd	3.6, 11.0	68.00
4	5.45, dd	3.6, 1.7	66.70
5	4.38, ddd	1.7, 7.0	67.95
6A	4.10, dd	6.5, 11.0	—
6B	4.14, dd	6.0, 11.0	61.64
1′	4.00–4.10, m		63.38
2′	4.22, m		74.06
3′	4.00–4.10, m		63.66
6 × Me (Ac) groups	1.98, 2.02, 2.053, 2.057, 2.08, 2.12		20.61, 20.61, 20.64, 20.64, 20.69, 20.83
6 × O-C (Ac) groups			169.96, 170.12, 170.31 170.31, 170.42, 170.42

longed to orthorhombic space group $P2_12_12_1$ with $a = 11.429$ Å, $b = 8.373$ Å, $c = 13.716$ Å. The structure was solved by direct methods and refined by full-matrix least-squares procedure to a standard crystallographic residual of 0.051 for the observed data (1556). A perspective drawing of the final X-ray model is given in Figure 1. Hydrogens are omitted for clarity. The absolute configuration was assumed by comparing the sign of optical rotation with that reported in the literature for the synthetic compound (6). Atomic coordinates and isotropic thermal parameters for **1** are given in Table 2.

While 2-*O*-α-D-galactopyranosyl glycerol hexaacetate [**1**] had previously been synthesized, mp 101–102°, $[\alpha]_D$ +113° (c = 0.9, Me_2CO) (6), this is the first report of its isolation from a natural source. The effect of compound **1** on mean arterial pressure in anesthetized rats has been studied. No significant effect was measured at a dose of 50 μg/kg, although the dose of 100 μg/kg showed

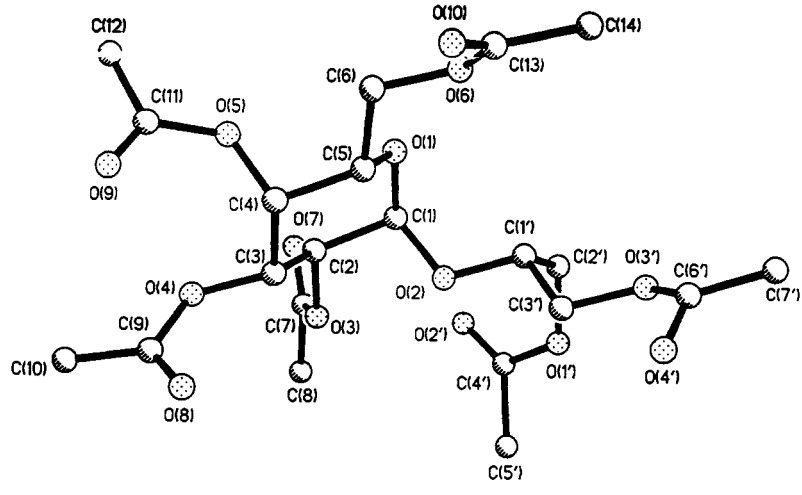

FIGURE 1. A computer-generated perspective drawing of the final X-ray model of compound **1**. Hydrogens are omitted for clarity.

TABLE 2. Atomic Coordinated ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($Å^2 \times 10^3$).

	x	y	z	U (eq)[a]
C-1	1165(6)	−2450	3218(5)	44(3)
C-2	1368(5)	−2642(12)	2136(4)	41(2)
C-3	2691(6)	−2673(12)	2076(4)	44(3)
C-4	3283(5)	−3954(11)	2760(5)	45(3)
C-5	3011(6)	−3700(12)	3784(5)	47(3)
C-6	3533(7)	−4945(13)	4501(5)	64(3)
C-7	−225(8)	−1585(16)	1022(6)	69(4)
C-8	−605(8)	−220(15)	378(6)	103(5)
C-9	3737(8)	−2454(15)	714(5)	62(3)
C-10	3772(8)	−3036(17)	−310(5)	96(4)
C-11	3438(8)	−6410(14)	1884(6)	66(3)
C-12	2854(9)	−7960(15)	1624(8)	102(5)
C-13	4226(8)	−4545(18)	6185(6)	91(4)
C-14	3942(7)	−4047(17)	7161(5)	97(4)
C-1′	1312(6)	−551(14)	4530(5)	54(3)
C-2′	93(7)	138(14)	4494(6)	67(3)
C-3′	2287(7)	576(15)	4939(6)	81(4)
C-4′	−492(9)	1636(17)	3044(8)	81(4)
C-5′	−355(9)	3276(16)	2600(8)	114(5)
C-6′	3020(9)	1257(19)	6554(7)	97(5)
C-7′	2893(9)	1560(19)	7553(7)	126(6)
O-1	1759(3)	−3679(10)	3799(3)	44(2)
O-2	1550(4)	−923(10)	3555(3)	45(2)
O-3	853(4)	−1327(11)	1549(3)	53(2)
O-4	2768(4)	−3035(11)	1061(3)	50(2)
O-5	2815(4)	−5506(10)	2434(3)	52(2)
O-6	3358(5)	−4481(12)	5475(3)	75(2)
O-7	−761(5)	−2797(12)	1076(5)	88(3)
O-8	4453(5)	−1631(12)	1185(4)	81(3)
O-9	4319(6)	−5970(12)	1618(5)	97(3)
O-10	5146(8)	−4917(26)	6045(5)	290(12)
O-1′	12(5)	1638(11)	3996(5)	75(2)
O-2′	−980(5)	500(13)	2633(5)	91(3)
O-3′	2171(6)	945(14)	5941(5)	123(4)
O-4″	3704(18)	−107(31)	6386(15)	140(10)
O-4′	3953(7)	1780(16)	6257(7)	84(4)

[a]Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

increased blood pressure initially and then became lethal. In a very recent study a series of diacylglycerol glycosides has been isolated from a blue-green alga and showed pronounced AIDS-antiviral activity in a tetrazolium-based microculture assay (7).

EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—The uv spectra were recorded on a Hitachi U-3200 spectrometer. Ir spectra were measured in $CHCl_3$ with a JASCO IRA-I spectrophotometer. The fdms was scanned on an MAT-312 mass spectrometer. All nmr experiments were done in $CDCl_3$ on a Bruker 400 & 110.61 MHz apparatus. X-ray diffraction studies were done on a Nicolet R3m/V diffractometer. Crystallographic calculations were done on Micro Vax II computers using SHELXTL PLUS structure solving software package (8).

PLANT MATERIAL AND ISOLATION.—*R. brittoniana* was collected from the surroundings of Karachi University campus in September 1987. The plant was identified by Mr. A. Ghafoor, Department of Botany, University of Karachi. A specimen has been deposited in the department's herbarium.

The whole plant (12 kg) was cut into pieces and percolated in MeOH. The extract so obtained was concentrated under reduced pressure, which gave a dark-colored residue to which H_2O was added. The insoluble material was removed by filtration

through Celite. The aqueous filtrate was shaken with petroleum ether (40–60°), and the organic-soluble portion was discarded. The aqueous phase was extracted with EtOAc and later with H_2O-saturated *n*-BuOH. The *n*-BuOH extract was evaporated at reduced pressure, and the residue (20 g) was subjected to Si gel cc. The column was eluted first with pure CH_2Cl_2 and then with CH_2Cl_2/MeOH gradients from 9:1 to pure MeOH. The fraction eluted with CH_2Cl_2-MeOH (9:1) yielded needle-shaped crystals of **1** (30 mg): mp 98°; $[\alpha]_D$ 62° ($CHCl_3$); uv λ max (MeOH) 205 nm; ir ν ($CHCl_3$) 2850 (C-H), 1720 (C=O), 1080 (C-O-C) cm^{-1}; ^1H nmr ($CDCl_3$, 300 MHz) see Table 1; ^{13}C nmr ($CDCl_3$, 100 MHz) see Table 1; eims *m/z* $[M]^+$ 506 ($C_{21}H_{30}O_{14}$).

X-RAY DIFFRACTION STUDIES.[1]—Crystal data: $C_{21}H_{30}O_{14}$, MW = 506, orthorhombic, space group $P2_12_12_1$, $a = 11.429$ Å, $b = 8.373$ Å, $c = 13.716$ Å (from 30 orientation reflections, $25° < \theta < 45°$). $V = 1297$ (7) Å^3, $Z = 4$, $D_c = 1.29$ g/cm^3, radiation CuKα (λ = 1.5418 Å). Crystal dimensions: 0.2 × 0.3 × 0.35 mm. Intensity data: $\theta = 2\theta$ scan type, $2\theta = 0.0$ to 112.0°, graphite monochromator, yielded 1831 reflections, out of which 1556 [$|F_o| \geq 4.0\ \sigma(F_o)$] were judged observed. The structure was solved by direct methods and refined by full-matrix least-squares methods for a final discrepancy index of 0.051. The atom O-4 appeared as disordered and its occupancy was included at their calculated positions (8).

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[1]Atomic coordinates for this structure have been deposited with the Cambridge Crystallographic Data Centre and can be obtained on request from Dr. Olga Kennard, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, UK.