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# *ENT*-16α,17,19-KAURANETRIOL-17-*O*,19-*O*-DI-*O*-β-D-GLUCOPYRANOSIDE, A NEW GLYCOSIDE FROM *TURBINA CORYMBOSA*

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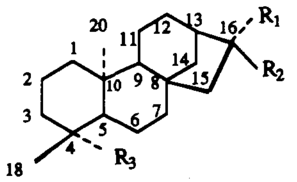
ABSTRACT.—A new glycoside, the 17-*O*,19-*O*-di-*O*-β-D-glucopyranoside of *ent*-16α,17,19-kauranetriol (epicorymbosin) [**1**], has been isolated from *Turbina corymbosa*, a plant used in ritual practices in Mexico and known as ololiuqui.

The first two glycosides isolated from *Turbina corymbosa* (L.) Raf. (Convolvulaceae) seeds were described in 1960 by Perezamador and Herrán (1). Lysergic-acid-related hallucinogenic alkaloids were found by A. Hofmann and Tscherter (2) in the same seeds. The structure of corymbosin [**3**] was established by García *et al.* (3,6), using $^{13}$C-nmr spectroscopy, as *ent*-16β,17,19-kauranetriol-17-*O*,19-*O*-di-*O*-β-D-glucopyranoside [**3**]. This compound was found to have gibberellic acid activity (4). We have isolated a new glucoside, $C_{32}H_{54}O_{13}$, an isomer of corymbosin. The ir and $^{1}$H-nmr spectra of **1** are similar but not identical to those of corymbosin. $^{13}$C nmr of **1** shows important differences from corymbosin [**2**] (Table 1). In particular, the carbon atoms of the glucose units in positions 17 and 19 show minor differences except for the anomeric carbons. However, there are relatively large differences for the $^{13}$C-nmr chemical shift values; the largest corresponds to C-5 which shifts upfield 8.1 ppm from corymbosin to epicorymbosin; C-17 shifts 6.3 ppm upfield, and C-18 shifts 9.6 ppm downfield. These large shifts were difficult to explain; however, using molecular models it became apparent that in epicorymbosin the sugar units are able to form up to three intramolecular hydrogen bonds, which considerably reduces freedom of motion for both sugar moieties, while this is not possible in corymbosin. The assignment of C-17 and C-19 is in agreement with the observed $^{13}$C-nmr and $^{1}$H-nmr spectra, and their correlation was determined through partial $^{1}$H decoupling experiments. For example, the signal at 104.5 ppm in the $^{13}$C spectrum of **1** was correlated to the anomeric hydrogen at 4.13 ppm and was assigned to the glucose linked to C-17. The $^{1}$H-$^{1}$H COSY experiment was useful to distinguish between the two AB patterns that correspond to the oxymethylene bridges at C-17 and C-19 in the $^{1}$H nmr of the octaacetate **3**, since in this case the hydrogens at C-17 (3.58, 4.05) and C-19 (3.17, 3.38) appear as distinctive signals with large chemical shifts; they show up as doublets with the expected correlation between geminal protons. The main observed nOe's for compound **3** are shown in Figure 1. Irradiation of the hydrogens at 0.74 or 0.98 ppm (C-20 and C-18) shows nOe's (7 and 4%, respectively) for



**1** $R_1=R_3=CH_2$-O-Glc, $R_2=OH$

**2** $R_1=OH$, $R_2=R_3=CH_2$-O-Glc

**3** $R_1=R_3=CH_2$-O-Glc Ac, $R_2=OH$

**4** $R_1=OH$, $R_2=R_3=CH_2$-O-Glc Ac

Glc=β-D-glucopyranoside

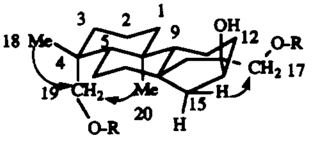
Glc Ac=β-D-glucopyranoside peracetate

TABLE 1. $^{13}$C-nmr Chemical Shifts For Compounds **1**–**4**.

| Carbon | Compound | | | |
|---|---|---|---|---|
| | **1** | **2**[a] | **3** | **4**[a] |
| C-1 | 40.3 t | 40.4 | 39.7 | 40.3 |
| C-2 | 18.0 t | 18.7 | 18.2 | 18.2 |
| C-3 | 35.4 t | 35.9 | 35.5 | 36.4 |
| C-4 | 36.9 s | 37.6 | 37.1 | 37.7 |
| C-5 | 48.2 d | 56.2 | 49.1 | 56.4 |
| C-6 | 19.9 t | 20.4 | 20.8 | 20.3 |
| C-7 | 41.0 t | 42.3 | 41.4 | 42.2 |
| C-8 | 44.0 s | 44.0 | 44.6 | 44.5 |
| C-9 | 56.0 d | 56.3 | 56.7 | 56.6 |
| C-10 | 38.7 s | 38.8 | 39.1 | 39.2 |
| C-11 | 17.9 t | 17.9 | 18.1 | 18.1 |
| C-12 | 26.1 t | 27.7 | 26.6 | 26.1 |
| C-13 | 45.1 d | 45.1 | 45.8 | 45.8 |
| C-14 | 36.8 t | 36.7 | 37.0 | 37.0 |
| C-15 | 52.3 t | 52.2 | 52.5 | 52.4 |
| C-16 | 79.5 s | 79.5 | 80.4 | 80.4 |
| C-17 | 77.9 t | 71.6 | 71.3 | 71.2 |
| C-18 | 18.1 q | 27.7 | 29.7 | 27.5 |
| C-19 | 74.0 t | 73.7 | 74.1 | 74.1 |
| C-20 | 17.5 q | 17.7 | 17.5 | 17.8 |
| Glucose at C-17 | | | | |
| C-1 | 104.5 d | 104.5 | 101.4 | 101.4 |
| C-2 | 73.7 d | 73.8 | 72.9 | 72.8 |
| C-3 | 76.8 d | 76.9 | 78.7 | 78.7 |
| C-4 | 70.1 d | 70.1 | 68.5 | 68.6 |
| C-5 | 76.3 d | 76.3 | 71.8 | 71.6 |
| C-6 | 61.1 t | 61.1 | 62.1 | 62.1 |
| Glucose at C-19 | | | | |
| C-1 | 103.7 d | 103.7 | 100.9 | 101.1 |
| C-2 | 73.4 d | 73.7 | 72.6 | 71.8 |
| C-3 | 76.8 d | 76.2 | 78.7 | 78.7 |
| C-4 | 70.1 d | 70.1 | 68.4 | 68.4 |
| C-5 | 76.9 d | 76.8 | 71.5 | 71.6 |
| C-6 | 61.1 t | 61.1 | 62.1 | 62.1 |

[a] Values for these compounds are from García Jiménez *et al.* (3) and García *et al.* (6).

the signals assigned to the hydrogens on C-19. On the other hand irradiation of the C-13 or C-15α hydrogens causes nOe's (3% each) for the signals assigned to C-17 hydrogens. An APT experiment for epicorymbosin [**1**] showed the expected singlets for C-4, C-10, C-8, and C-13 as well as a highly displaced singlet at 79.5 ppm for C-16, in good agreement with a tetracyclic diterpene structure isomeric with corymbosin. Doublets were observed for C-5, C-9, and C-13 as well as for most sugar carbon atoms except for C-6′ and C-6″ which appear as a triplets; prominent are two doublets at 104.5 and 103.7 that correspond to anomeric carbons at C-1′ and C-1″. There are triplets for C-1, C-2, C-3, C-6, C-7, C-11, C-12, C-14, and C-15 in addition to those already mentioned. Fi-



R=Glc Ac

FIGURE 1. NOe's of Compound **3**.

nally there are two quartets for the two methyl groups at C-20 and C-18 (multiplicities observed in a $^{13}C$ hydrogen undecoupled spectrum). The $^{13}C$ nmr of the acetate derivative **3** allows assignment of nine free hydroxy groups, since the substance forms an octaacetate, and help to establish that the hydroxy groups at C-2, C-3, C-4, and C-6 of both sugar units are free in the original glucoside. The tertiary hydroxy group at C-16 in the molecule remains unacetylated. The above information is consistent with structure **1** for the title compound.

## EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURE.—Melting points were determined in a Fisher-Johns melting point apparatus and are uncorrected. The ir spectrum was recorded on a Nicolet 5SX spectrophotometer. The $^{1}H$- and $^{13}C$-nmr spectra were measured in a Varian 300 MHz spectrometer using TMS as an internal standard. Pre-coated Si gel plates (Kieselgel 60 $F_{254}$, 0.25 mm thickness, Merck) were used for analytical tlc. Compounds were detected by spraying with acidic cerium sulfate (saturated solution of ceric sulfate in 65% $H_2SO_4$). The crude glycosides were obtained by MeOH extraction from *T. corymbosa* seeds as previously described (4,5). The plant material was collected in 1989 in San Carlos Yautepec, state of Oaxaca, and identified as *T. corymbosa* by comparison with a specimen at Instituto de Biología UNAM (MEXU) herbarium. A voucher specimen is kept at the herbarium in Facultad de Ciencias UNAM (FCME).

ent-*16α17,19-Kauranetriol-17*-O,*19*-O-*di*-O-β-D-*glucopyranoside* [**1**].—Compound **1** was separated from **2** and other glycosides by fractional crystallization using MeOH-iPrOH (1:1), further purified by preparative tlc using the upper phase from *n*-BuOH–$H_2O$–HOAc (10:9:1), and recrystallized using iPrOH (mp 260–262°). Compound **1** was crystallized from MeOH: mp 261–262°, $[\alpha]^{25}$D −60° ($c$ = 0.0025 in MeOH), $R_f$ 0.62 [*n*-BuOH–HOAc–$H_2O$ (5:1:1)] ($C_{32}H_{54}O_{13}$ requires C 59.43, H 8.41, O 32.16; found C 59.40, H 8.41, O 32.15); ir (KBr) ν max $cm^{-1}$ 3500, 2920, 2930, 1600, 1430, 1374, 1283, 1160, 1090, 1068, 1017, 990, 870, 710, 682, 603, 508; $^{1}H$ nmr (300 MHz, DMSO-$d_6$) δ (ppm) 0.71 (3H, s, Me-18), 0.99 (3H, s, Me-20), 1.72 and 1.80 (2H, d, $J$ = 13, $CH_2$-15), 1.94 (1H, broad s, CH-13), 2.98 and 3.03 (2H, m, m, CH-2 glucose at C-19 and C-17), 3.07 (2H, m, CH-4 both glucose units), 3.11 (2H, m, CH-5 both glucose units), 3.33 (2H, dd, $J$ = 9, CH-3 both glucose units), 3.44 and 3.63 (4H, m, m, $CH_2$-6 both glucose units), 4.03 and 4.14 (2H, d, $J$ = 7.7, CH-1 glucose at C-19 and C-17, respectively), 4.47 and 4.50 (2H, t, $J$ = 8, OH at C-6 of both glucose units), 4.82 (1H, d, $J$ = 5, OH), 4.88 (1H, s, OH at C-16), 4.89 (1H, d, $J$ = 4, OH), 4.90 (1H, d, $J$ = 5, OH), 4.92 (1H, d, $J$ = 5, OH), 4.94 (1H, d, $J$ = 4, OH), 5.12 (1H, d, $J$ = 4, OH); fdms (70 eV) *m/z* $[M + Na]^+$ 669.

ent-*16α,17,19-Kauranetriol-17*-O,*19*-O-*Di*-O-β-D-*Glucopyranoside octaacetate* [**3**].—This compound was prepared from **1** by the usual procedure (7) using pyridine and $Ac_2O$. After the usual isolation procedure the octaacetate was purified by Si gel cc using EtOAc as the eluent: mp 194–195°; $[\alpha]^{20}$D −23.1° ($c$ = 0.1, $CHCl_3$); ir (KBr) ν max $cm^{-1}$ 3400, 1730, 1360, 1190, 1030; $^{1}H$ nmr ($CDCl_3$) δ (ppm) 0.74 (3H, s, Me-20), 0.98 (3H, s, Me-18), 1.73, 1.80 (2H, d, $J$ = 13, $CH_2$-15), 2.01, 2.02, 2.02, 2.03, 2.03, 2.05, 2.08, 2.09 (24H, s, 8 acetyl Me-); 3.17 and 3.38 (2H, d, $J$ = 12, $CH_2$-19); 3.69 (2H, ddd, $J$ = 3, $J$ = 5.8, $J$ = 9, CH-5, both glucose units), 3.58 and 4.05 (2H, d, $J$ = 13, $CH_2$-17), 4.15 and 4.24 (4H, ddd, $J$ = 2 and 13, $J$ = 4 and 13, $CH_2$-6, both glucose units), 4.42 (1H, d, $J$ = 7.8, CH-glucose at C-19), 4.56 (1H, d, $J$ = 7.8, CH- glucose at C-17) 5.02 and 5.03 (2H, d, d, $J$ = 8 and 9.5, CH-2, both glucose units), 5.09 and 5.10 (2H, d, d, $J$ = 9.5 and 9, 5, CH-4, both glucose units), 5.18 and 5.21 (2H, d, d, $J$ = 9.5 and 9.5, CH-3, both glucose units).

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