143. Two New Antifungal Naphthoxirene Derivatives and their Glucosides from *Sesamum angolense* WELW.

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Two novel naphthoxirene derivatives **1** and **2** and their glucosides **3** and **4** have been isolated from the root bark of *Sesamum angolense* WELW. (Pedaliaceae) by preparative liquid chromatography. The structure of **1** was established by X-ray diffraction analysis. The identities of the other naphthoxirenes were deduced by spectroscopic (IR, UV, ^{1}H-NMR, ^{13}C-NMR, EI-MS, DCI-MS) and chemical methods (oxidation, acid and enzymatic hydrolysis). Compounds **1**–**3** exhibited antifungal activity. Naphthoxirene **1** was, in addition, cytotoxic to human colon carcinoma cells.

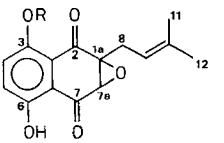
Introduction. – *Sesamum angolense* WELW. (Pedaliaceae) is a wild herb growing in tropical Africa which has several uses in African traditional medicine. The roots are employed to hasten delivery of babies, the stems for their antihemorrhagic and painkilling properties after tooth removal, and the leaves are utilized to cure smallpox and as a soap substitute [1].

Previous phytochemical studies on the genus *Sesamum* have been almost exclusively confined to *Sesamum indicum* L. A flavonoid [2] and several lignans [3] [4] have been isolated from this species; phenolic acids have been identified [5] [6], and the presence of saponins and alkaloids has also been reported [7] [8]. Very little is known about the constituents of *S. angolense*. Only the occurrence in the seeds of the lignans sesamin, sesamolin, and sesangolin has been previously reported [3] [9].

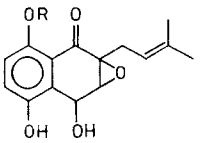
During preliminary screening, the CH_2Cl_2 extract of the root bark of *S. angolense* exhibited antifungal activity against *Cladosporium cucumerinum*, a plant pathogenic fungus, as well as cytotoxicity towards human colon cancer cells.

Here, we report the isolation and structure elucidation of the antifungal constituents from the root bark which were shown to be new naphthoxirene derivatives. One of them also possessed cytotoxic properties and was responsible for the antiproliferative activity of the CH_2Cl_2 extract.

Results. – The root bark of *S. angolense* collected in Malawi was extracted successively with CH_2Cl_2 and MeOH. The bio-active CH_2Cl_2 extract was fractionated by flash chromatography on silica gel with $CHCl_3$ and $CHCl_3$/MeOH mixtures of increasing polarity. Fifteen fractions were collected (I-XV). Crystallisation of *Fraction II* and *XI* provided compounds **1** and **3**, respectively. Low-pressure liquid chromatography on *RP-8* of *Fraction VIII* allowed the isolation of **2**. Fractionation of the inactive MeOH



1 R = H
3 R = β-D-glucopyranosyl



2 R = H
4 R = β-D-glucopyranosyl

extract was also carried out; droplet counter-current chromatographic (DCCC) separation with the solvent system $CHCl_3$/MeOH/i-PrOH/H_2O 5:6:1:4 in the ascending mode, followed by low-pressure liquid chromatography on *RP-8* afforded **4**.

Crystals of **1**, grown from heptane as yellow blocks, were submitted to an X-ray diffraction analysis (see *Exper. Part*). The structure was, thus, established as 3,6-dihydroxy-1a-(3-methyl-2-butenyl)naphth[2,3-*b*]oxirene-2,7(1a*H*, 7a*H*)-dione, a new naphthoquinone epoxide. A view of **1** is given in the *Fig.* Distances and angles in the molecule

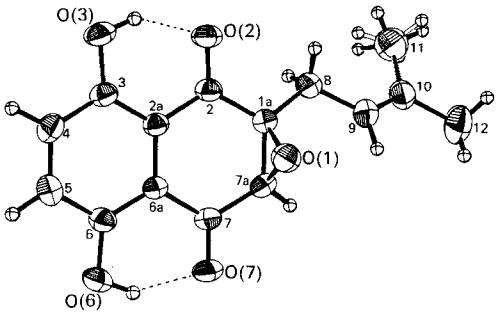


Figure. *View of the molecule* **1** *showing the atomic numbering scheme and the vibrational ellipsoids* (50% probability level)

are normal *(Table 1)*. The quinone ring has a flat boat conformation with C(2) and C(7) both displaced by 0.100(2)Å from the best plane through C(1a), C(2a), C(6a), and C(7a) (planar to within 0.008(3)Å) and on the opposite side of the molecule from the epoxide O-atom O(1). The phenyl ring is planar to within 0.007(3) Å. The epoxide ring angles range from 59.1(1)° at C(1a) to 61.3(1)° at O(1). C(12), C(11), C(10), C(9), and C(8) are planar to within 0.009(3)Å and make a dihedral angle of 39.3° with the best plane through C(1a), C(2a), C(6a), and C(7a). There are two strong intramolecular H-bonds between hydroxy O(3) and the carbonyl O(2) and hydroxy O(6) and the carbonyl O(7) *(Table 1)*. There is only one short intermolecular contact between non-H-atoms, and that is between O(3) and O(7) of a molecule displaced in the plane [001]. This cannot be an intermolecular H-bond as angle O(3)–H(03)···O(7) is only 49.5°. The conformation is similar to the one which has been recently published for naphth[2,3-*b*]oxirene-2,7(1a*H*, 7a*H*)-dione [10].

Spectroscopic data of **1** were in good agreement with those found for the 3-hydroxy and 6-hydroxy analogues synthetically prepared by *Matsumoto et al.* [11]. The structures of the other compounds were deduced by spectroscopic and chemical methods.

Table 1. *Bond Distances* [Å] *and Angles* [°]

Distance		Distance		Angle		Angle	
O(1)–C(1a)	1.447(3)	C(4)–C(5)	1.366(3)	C(1a)–O(1)–C(7a)	61.3(1)	C(4)–C(5)–C(6)	120.3(2)
O(1)–C(7a)	1.439(3)	C(5)–C(6)	1.397(3)	O(1)–C(1a)–C(2)	110.6(2)	O(6)–C(6)–C(5)	116.7(2)
C(1a)–C(2)	1.503(3)	C(6)–O(6)	1.351(3)	O(1)–C(1a)–C(7a)	59.1(1)	O(6)–C(6)–C(6a)	123.4(2)
C(1a)–C(7a)	1.471(3)	C(6)–C(6a)	1.394(3)	C(2)–C(1a)–C(7a)	117.4(2)	C(5)–C(6)–C(6a)	119.9(2)
C(1a)–C(8)	1.503(3)	C(6a)–C(7)	1.466(3)	O(1)–C(1a)–C(8)	117.4(2)	C(2a)–C(6a)–C(6)	119.7(2)
C(2)–O(2)	1.222(3)	C(7)–O(7)	1.226(3)	C(2)–C(1a)–C(8)	115.6(2)	C(2a)–C(6a)–C(7)	120.5(2)
C(2)–C(2a)	1.471(3)	C(7)–C(7a)	1.490(3)	C(7a)–C(1a)–C(8)	123.2(2)	C(6)–C(6a)–C(7)	119.8(2)
C(2a)–C(3)	1.394(3)	C(8)–C(9)	1.505(3)	O(2)–C(2)–C(1a)	118.7(2)	O(7)–C(7)–C(6a)	123.1(2)
C(2a)–C(6a)	1.424(3)	C(9)–C(10)	1.316(4)	O(2)–C(2)–C(2a)	121.8(2)	O(7)–C(7)–C(7a)	118.3(2)
C(3)–O(3)	1.346(3)	C(10)–C(11)	1.503(5)	C(1a)–C(2)–C(2a)	119.5(2)	C(6a)–C(7)–C(7a)	118.6(3)
C(3)–C(4)	1.400(3)	C(10)–C(12)	1.511(4)	C(2)–C(2a)–C(3)	119.1(2)	O(1)–C(7a)–C(1a)	59.6(1)
O(3)–H(03)	0.89(4)	O(6)–H(06)	0.91(4)	C(2)–(2a)–C(6a)	121.5(2)	O(1)–C(7a)–C(7)	113.6(2)
H(03)···O(2)	1.78(4)	H(06)···O(7)	1.83(4)	C(3)–C(2a)–C(6a)	119.3(2)	C(1a)–C(7a)–C(7)	121.3(2)
O(3)···O(2)	2.578(4)	O(6)···O(7)	2.622(2)	O(3)–C(3)–C(2a)	123.3(2)	C(1a)–C(8)–C(9)	115.7(2)
H(03)···O(7)[a])	2.30(4)			O(3)–C(3)–C(4)	117.1(2)	C(8)–C(9)–C(10)	124.7(3)
O(3)···O(7)[a])	2.776(3)			C(2a)–C(3)–C(4)	119.5(2)	C(9)–C(10)–C(11)	123.0(3)
				C(3)–C(4)–C(5)	121.2(2)	C(12)–C(10)–C(9)	121.5(3)
				O(3)–H(03)···O(2)	147.1(6)	C(12)–C(10)–C(11)	115.6(3)
				O(3)–H(03)···O(7)[a])	49.5(1.9)	O(6)–H(06)···O(7)[a])	143.8(6)

[a]) $1 - x, 1 + y, z$.

The EI-MS of **2** showed a molecular ion at *m/z* 276, *i.e.* 2 amu greater than **1**. The ^{13}C-NMR and DEPT data suggested that **2** was a partially reduced analogue of **1**. Furthermore, in the ^{1}H-NMR spectrum of **2**, the signal for the epoxide proton H–C(7a), instead of being a *s* as observed for **1**, appeared as a *d* at 3.85 ppm coupling with new signal at 5.48 ppm attributed to H–C(7) (J = 2.4 Hz). Thus, it could be unequivocally established that the carbonyl group at C(7) was reduced. The structure of **2** is, therefore, 7,7a-dihydro-3,6,7-trihydroxy-1a-(3-methyl-2-butenyl)-naphth[2,3-*b*]oxiren-2(1a*H*)-one, the corresponding dihydronaphthoquinone epoxide of **1**.

The MS (DCI) of **4** (reactant gas NH_3, positive-ion mode) showed quasimolecular ions at *m/z* 456 ($[M + NH_4]^+$) and 439 ($[M + H]^+$). Additional signals at *m/z* 294 ($[(M + NH_4) - 162]^+$) and 277 ($[(M + H) - 162]^+$) corresponded to the loss of a hexosyl unit. Acid hydrolysis yielded glucose, but led to the decomposition of the aglycone. Enzymatic hydrolysis with β-D-glucosidase provided the aglycone which was idcntified as **2** by TLC, HPLC, and ^{1}H-NMR. The ability of β-D-glucosidase to cleave the glucosyl residue confirmed the β-D-pyranosyl configuration of the glucose, inferred at first from ^{1}H- and ^{13}C-NMR data. Determination of the attachment position of the glucose moiety was realized by comparison of the UV spectra of aglycone **2** and glucoside **4** before and after addition of $AlCl_3$ [12]. Thus, the peak at 379 nm in the UV spectrum of aglycone **2** was shifted bathochromically to 461 nm, because of the HO–C(3) *peri* to the carbonyl group. Under the same conditions, no shift was measured for glucoside **4**, indicating substitution at HO–C(3). Compound **4** was, thus, the 3-*O*-β-D-glucoside of **2**. The absence of a signal for a chelated phenolic OH in the ^{1}H-NMR spectrum of **4** and the upfield shift of 4.6 ppm (compared with **2**) for the carbonyl resonance in the ^{13}C-NMR spectrum confirmed the attachment position of glucose at HO–C(3) in **4**.

In a similar manner (by DCI-MS, ^{1}H- and ^{13}C-NMR, acid and enzymatic hydrolysis), it was established that **3** was a β-D-glucopyranoside of **1**. However, a determination of the position of attachment of the glucose based on spectroscopic data was in this case very difficult because of the symmetry of the aromatic moiety of aglycone **1**. In the ^{13}C-NMR spectrum of **1**, signals for C(2), C(2a), C(3), and C(4) could indeed be interchanged with those for C(7), C(6a), C(6), and C(5), respectively. Attribution of the chemical shifts of the phenolic OH in the ^{1}H-NMR spectrum was hazardous, and the 2 aromatic protons gave rise to an unresolved *s*. The problem was finally solved by oxidation of glucoside **4** with potassium dichromate. The oxidation product was identified as glucoside **3** by TLC, HPLC, and ^{1}H-NMR, which led to the conclusion that the glucose was attached to the same OH group (*i.e.* HO–C(3)) in both **3** and **4**. Compound **3** is thus the 3-*O*-β- D-glucoside of **1**. This also confirmed that compounds **3** and **4**, and consequently **1** and **2**, differed only in the oxidation state of C(7).

Compounds **1**–**4** were tested for their fungitoxicity against *Cladosporium cucumerinum* using a TLC bioassay [13]. In this assay, 0.5 μg of naphthoxirene **1** was sufficient

to prevent growth of the fungus. Naphthoxirene **2** and glucoside **3** when spotted onto the plate in 5 µg amounts also proved to be fungicidal, but 50 µg of glucoside **4** were inactive. The cytotoxicity of the compounds towards Co-115 colon tumour cells was also investigated. The cell numbers were measured after a 5 day incubation period, using a spectrophotometric assay [14]. Only naphthoxirene **1** exhibited cytotoxic properties (LD_{50} 0.35 µg/ml). In fact, **1** was shown to be responsible for the antiproliferative activity of the crude CH_2Cl_2 extract (LD_{50} 0.875 µg/ml).

Discussion. – Naphthoquinone epoxides are rather uncommon plant constituents. In fact, diosquinone and batocanone isolated from *Diospyros* species (Ebenaceae) [15] [16] are the only naphthoquinone epoxides previously known to occur in higher plants. Additionally, the structurally related compounds frenolicin [17], nanaomycin E, αE, and βE [18] [19] as well as the dihydronaphthoquinone epoxides mycochrysone [20] and cervicarcin [21] have been reported from microorganisms. Compounds **3** and **4** are of particular interest as they are, to our knowledge, the first example of glycosides in this class of substances. Aglycones **1** and **2** are not formed as artefacts during the isolation procedure by cleavage of their glucosides since they are present in the crude CH_2Cl_2 extract. However, it cannot be ruled out that such a scission arises during the drying of the plant material.

The fungicidal activity of **1**–**4** seems to require the presence in the molecule of an OH in *peri* position to a carbonyl function. Naphthoxirene **1** in which two such functional groups are present exhibits the strongest activity; compounds **2** and **3** which contain only one OH *peri* to a carbonyl are about 10 times less active and glucoside **4** which does not possess this arrangement is inactive. It is interesting to notice that naphthoxirene **1** which exhibits the strongest fungicidal activity is also the only one with cytotoxic properties.

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Experimental Part

General. DCCC: *Büchi 670 DCC* chromatograph (294 tubes; i.d. 2.7 mm). Prep. low-pressure liquid chromatography: *Lobar RP-8* column (40–63 µm; i.d. 2.5 × 27 cm; *Merck*, Darmstadt), equipped with a *Duramat-80* pump (*Chemie und Filter*, Regensdorf). HPLC: the purity of the compounds was checked by HPLC; *Spectra-Physics 8700* pump, *Rheodyne* injector, *LKB 2151* UV detector; 7 µm *RP-18* column (i.d. 4.6 × 250 mm; *Knauer*), MeOH/H_2O 75:25, 55:45, 50:50, and 30:70 for **1**, **2**, **3**, and **4**, resp.; detection at 220 or 254 nm. TLC: silica-gel precoated Al sheets *(Merck)*, $CHCl_3$/MeOH 85:15 (system 1) or $CHCl_3$/MeOH/H_2O 65:35:5 (system 2); *RP-8* precoated glass plates (HPTLC, *Merck*), MeOH/H_2O mixtures. M.p.: *Mettler FP 80/82* hot stage apparatus; uncorrected. UV: *Perkin Elmer Lambda 3* spectrophotometer. IR: *Perkin Elmer 781* spectrometer. ^{1}H- and ^{13}C-NMR: *Varian VXR-200* at 200 and 50.5 MHz, resp.; chemical shifts δ in ppm relative to TMS; DEPT experiments allowed distinction of the CH, CH_2, and CH_3 signals. EI-MS: *Nermag R 1030*. Desorption-chemical-ionization (DCI) MS: *Ribermag R10-10B* quadrupole instrument with NH_3 as reactant gas.

Plant Material. S. angolense was collected near Kasungu (Malawi). A voucher specimen of the plant material is retained at the herbarium, Chancellor College, University of Malawi, Zomba.

Extraction and Isolation. The powdered root bark of *S. angolense* (121 g) was extracted at r.t. with CH_2Cl_2, followed by MeOH. A 1.5-g portion of the CH_2Cl_2 extract (3.0 g) was submitted to flash chromatography on a silica-gel column (63–200 µm; i.d. 2.4 × 48 cm) with $CHCl_3$ (1 l), $CHCl_3$/MeOH 95:5 (1.6 l), and $CHCl_3$/MeOH *85:15 (1.3 l)*, and 15 fractions were collected. Repeated crystallisations of *Fraction II* (162 mg) in heptane provided **1** (42 mg) in pure form. Compound **2** (18 mg) was obtained from *Fraction VIII* (205 mg) by low-pressure liquid chromatography on *RP-8* with MeOH/H_2O 75:25. Recrystallisation of *Fraction XI* (113 mg) in $CHCl_3$/MeOH

1:1/hexane afforded **3** (68 mg). A portion (3 × 3.0 g) of the MeOH extract (14.4 g) was separated into 15 fractions by DCCC with $CHCl_3$/MeOH/i-PrOH/H_2O 5:6:1:4 in the ascending mode. Compound **4** (64 mg) was isolated from *Fraction XIV* (138 mg) by low-pressure liquid chromatography on *RP-8* with MeOH/H_2O 4:6.

Acid Hydrolysis. The glucoside **3** (1 mg) was refluxed in 2N HCl (10 ml) for 3 h. The mixture was extracted with Et_2O (2 × 10 ml) followed by BuOH (2 × 10 ml). The org. layers were checked by TLC for the aglycone. The aq. layer was adjusted to pH 5 with $NaHCO_3$. After evaporation, the sugar was extracted from the residue with pyridine (20 ml) and analysed by TLC on silica gel with AcOEt/MeOH/H_2O/AcOH 65:15:15:20; detection with *p*-anisidine phthalate.

Glucoside **4** (1 mg) was hydrolysed by the same procedure; for extraction, Et_2O was replaced by AcOEt.

Enzymatic Hydrolysis. Glucoside **3** (4 mg) and β-D-glucosidase (4 mg, 90 units) from almonds (*G-4511; Sigma Chemical,* St Louis) were dissolved in acetate buffer (10 ml) of pH 5.5. The mixture was kept at 36° for 2 h and extracted with CH_2Cl_2 (2 × 20 ml). The org. phase was washed with H_2O (2 × 10 ml) and evaporated to afford 2.1 mg of **1**.

Hydrolysis of **4** (10 mg) was carried out under the same conditions with β-D-glucosidase (20 mg, 110 units) from almonds *(G-8625; Sigma Chemical).* After stirring for 6 h, the mixture was extracted with CH_2Cl_2 (3 × 20 ml). The org. phase was washed with H_2O (2 × 20 ml) and evaporated to leave 4.6 mg of **2**.

Oxidation with Potassium Dichromate. A soln. of $K_2Cr_2O_7$ (8.3 mg) in 70% AcOH (1 ml) was added to a soln. of **4** (10 mg) in AcOH (9 ml). After 2½ h stirring at r.t., the mixture was poured into H_2O (100 ml), neutralized with conc. NH_3, and extracted with AcOEt (3 × 100 ml). The org. phase was washed with H_2O (100 ml) and evaporated to leave the crude product (5.5 mg). Purification by low-pressure liquid chromatography on a *Lobar RP-8* column (40–63 μm; i.d. 1.1 × 20 cm; *Merck*) with MeOH/H_2O 7:3 provided pure **3** (1 mg).

X-Ray Analysis. Suitable crystals of **1** were grown from heptane as yellow blocks. Crystal data: $C_{15}H_{14}O_5$, $M_r = 274$, space group $P2_12_12_1$, $a = 4.973(1)$, $b = 6.506(1)$, $c = 40.219(2)$ Å, $V = 1301.3$ Å^3, $F(000) = 396$, $Z = 4$, $D_x = 1.398$ gcm^{-3}, Mo$K\alpha$, $\lambda = 0.71073$ Å, $\mu = 0.51$ cm^{-1}. Size of crystal used for data collection, 0.27 × 0.42 × 0.42 mm. Preliminary *Weissenberg* and precession photographs indicated the crystals to be orthorhombic, space group $P2_12_12_1$. Intensity data were measured using a *Stoe-Siemens AED2* four circle diffractometer (graphite monochromated Mo$K\alpha$ radiation) using the ω/θ scan mode for $2.5° < \theta < 27.5°$. Three standard reflections measured every h showed no intensity variation. Cell parameters were refined from $\pm\omega$ values of 10 reflections and their equivalents in the range $30° < 2\theta < 40°$. There were 1775 unique reflections of which 1482 [$Fo > 3\sigma(Fo)$] were considered observed. No absorption or extinction corrections were applied. The structure was solved by direct methods using the SHELX-76 system [22] which was also used for all further calculations. All the H-atoms were located from difference *Fourier* syntheses and refined isotropically. Two alternative arrangements were observed for the CH_3(11) H-atoms. Full-matrix least-squares anisotropic refinement converged at $R = 0.038$, $R = 0.042$; $w^{-1} = \sigma^2|F_o| + 0.00102|F_o|^2$. Max. parameter shift/e.s.d. = 0.28, average parameter shift/e.s.d. < 0.05.

Table 2. *Final Positional and Equivalent Isotropic Thermal Parameters* (× 10^4). E.s.d. in Parentheses.

$$U_{eq} = 1/3 \sum_i \sum_j U_{ij} a_i^* a_j^* \bar{a}_i \bar{a}_j$$

Atom	*x/a*	*y/b*	*z/c*	U_{eq} (Å^2)	Atom	*x/a*	*y/b*	*z/c*	U_{eq} (Å^2)
O(1)	1089(4)	1205(3)	1522(0)	458(5)	C(5)	–2092(5)	–164(4)	296(1)	427(7)
O(2)	–885(4)	5493(3)	1125(0)	504(6)	C(6)	–3(5)	–759(4)	508(1)	376(6)
O(3)	–4162(4)	4687(3)	646(1)	529(6)	C(6a)	699(4)	481(3)	777(0)	325(6)
O(6)	1261(4)	–2539(3)	434(0)	492(6)	C(7)	2892(5)	–145(3)	998(1)	355(6)
O(7)	4314(4)	–1649(2)	945(0)	460(5)	C(7a)	3388(5)	1078(3)	1305(1)	390(7)
C(1a)	2036(5)	3059(3)	1361(1)	363(6)	C(8)	3174(6)	4718(4)	1580(1)	451(7)
C(2)	66(5)	3767(3)	1102(1)	356(6)	C(9)	4926(6)	3994(4)	1862(1)	472(8)
C(2a)	–683(5)	2369(3)	830(0)	333(6)	C(10)	6524(6)	5186(4)	2037(1)	490(8)
C(3)	–2740(5)	2939(3)	613(1)	369(6)	C(11)	6830(10)	7448(6)	1972(1)	708(13)
C(4)	–3428(5)	1641(4)	349(1)	411(7)	C(12)	8187(9)	4346(7)	2321(1)	719(13)

Heights in final difference synthesis +0.17 to –0.16 e·Å^{-3}. Atomic scattering factors from [23]. Final positional and equivalent isotropic thermal parameters are given in *Table 2,* bond distances and angles in *Table 1.* The numbering scheme used is apparent from the *Fig.* prepared using ORTEP [24]. Final observed and calculated structure factors and H-atom positions are available from *H. St-E.*

3,6-Dihydroxy-1a-(3-methyl-2-butenyl)naphth[2,3-b]oxirene-2,7(1aH, 7aH)-dione (**1**). Yellow blocks from heptane. M.p. 85–86°. TLC (SiO_2, system 1): R_f 0.77. UV (MeOH): 209 (18800), 236 (sh, 9500), 271 (5600), 413 (6800). UV (MeOH + $AlCl_3$): 212, 297, 464. IR (KBr): 1645, 1585, 1450, 1220, 1150. ^{1}H-NMR (C_6D_6): 11.94, 11.76 (2*s*, HO–C(3), HO–C(6)); 6.71 (*s*, H–C(4), H–C(5)); 4,94 (br. *t*, *J* = 7.6, H–C(9)); 3.49 (*s*, H–C(7a)); 2.77 (*dd*, *J* = 15.1, 7.9), 2.48 (*dd*, *J* = 15.1, 7.3, together 2H–C(8)); 1.55, 1.46 (2*s*, 3H–C(11), 3H–C(12)). ^{13}C-NMR (C_6D_6): 195.88, 195.25 (C(2), C(7)); 157.27, 156.84 (C(3), C(6)); 137.13 (C(10)); 129.20, 128.92 (C(4), C(5)); 115.71 (C(9)); 111.67, 111.61 (C(2a), C(6a)); 63.55 (C(1a)); 59.48 (C(7a)); 26.29 (C(8)); 25.80 (C(12)); 17.99 (C(11)). EI-MS: 274 (40), 259 (14), 256 (27), 245 (100), 241 (65), 227 (42), 203 (94).

7,7a-Dihydro-3,6,7-trihydroxy-1a-(3-methyl-2-butenyl)naphth[2,3-b]oxiren-2(1aH)-one (**2**). Yellow needles from toluene. M.p. 153–156° (dec.). TLC (SiO_2, system 1): R_f 0.47. UV (MeOH): 205 (14400), 242 (9800), 268 (6100), 379 (4600). UV (MeOH + $AlCl_3$): 205, 225, 258, 294, 461. IR (KBr): 3430, 3230, 1635, 1620, 1585, 1470, 1220. ^{1}H-NMR ((D$_6$)Acetone): 11.08 (br. *s*, HO–C(3)); 7.18 (*d*, *J* = 8.9, H–C(5)); 6.80 (*d*, *J* = 8.9, H–C(4)); 5.48 (*d*, *J* = 2.4, H–C(7)); 5.15 (br. *t*, *J* = 7.3, H–C(9)); 3.85 (*d*, *J* = 2.4, H–C(7a)); 2.91 (*dd*, *J* = 15.1, 8.1), 2,51 (*dd*, *J* = 15.1, 6.6, together 2H–C(8)); 1.70, 1.68 (2*s*, 3H–C(11), 3H–C(12)). ^{13}C-NMR ((D$_6$)Acetone): 200.78 (C(2)); 155.99 (C(3)); 148.68 (C(6)); 135.91 (C(10)); 126.65 (C(6a)); 126.27 (C(5)); 118.53, 117.87 (C(4), C(9)); 113.68 (C(2a)); 61.63, 61.22 (C(7), C(7a)); 60.08 (C(1a)); 27.28 (C(8)); 25.93 (C(12)); 18.07 (C(11)). EI-MS: 276 (39), 258 (39), 243 (89), 240 (40), 229 (37) 215 (39), 41 (100).

3-(β-D-Glucopyranosyloxy)-6-hydroxy-1a-(3-methyl-2-butenyl)naphth[2,3-b]oxirene-2,7-(1aH, 7aH)-dione (**3**). Yellow prisms from $CHCl_3$/MeOH 1:1/hexane. M.p. 110–112°. TLC (SiO_2, system 1): R_f 0.19. UV (MeOH): 208 (22100), 235 (10700), 261 (7600), 387 (5400). UV (MeOH + $AlCl_3$): 209, 288, 447. IR (KBr): 3420, 1695, 1660, 1465, 1070. ^{1}H-NMR ((D$_6$)Acetone; primed locants refer to the sugar moiety): 11.08 (br. *s*, HO–C(6)); 7.74, 7.22 (2*d*, *J* = 9.4, H–C(4), H–C(5)); 5.12 (br. *t*, *J* = 7.3, H–C(9)); 4.93 (*d*, *J* = 7.1, H–C(1′)); 4.5–4.2, 4.0–3.4 (2*m*, glucose protons, H–C(7a)); 2.94 (*dd*, *J* = 15.5, 8.0), 2.75 (*dd*, *J* = 15.5, 6.6, together 2H–C(8)); 1.72, 1.67 (2*s*, 3H–C(11), 3H–C(12)). ^{13}C-NMR ((D$_6$)Acetone): 198.20 (C(7)); 190.95 (C(2)); 157.02 (C(6)); 151.27 (C(3)); 136.85 (C(10)); 129.82 (C(4)); 125.16 (C(5)); 121.49 (C(2a)); 116.94 (C(9)); 115.01 (C(6a)); 103.24 (C(1′)); 77.97, 77.57 (C(3′), C(5′)); 74.42 (C(2′)); 71.15 (C(4′)); 64.29 (C(1a)); 62.58 (C(6′)); 60.20 (C(7a)); 26.46 (C(8)); 25.90 (C(12)); 18.10 (C(11)). DCI-MS (NH_3, positive ions): 454 ($[M + NH_4]^+$), 437 ($[M + H]^+$), 292 ($[(M + NH_4) - 162]^+$), 275 ($[(M + H) - 162]^+$), 245, 180.

3-(β-D-Glucopyranosyloxy)-7,7a-dihydro-6,7-dihydroxy-1a-(3-methyl-2-butenyl)naphth[2,3-b]oxiren-2(1aH)-one (**4**). Amorphous, white powder. M.p. 124–127°. TLC (SiO_2, system 1): R_f 0.05. TLC (SiO_2, system 2): R_f 0.47. UV (MeOH): 205 (16100), 231 (10900), 259 (sh, 4500), 337 (3700). UV (MeOH + $AlCl_3$): 205, 231 (sh), 259 (sh), 337. IR (KBr): 3380, 1680, 1590, 1260, 1075. ^{1}H-NMR ((D$_6$)Acetone; primed locants refer to the sugar moiety): 7.30, 7.07 (2*d*, *J* = 9.0, H–C(4), H–C(5)); 5.56 (*d*, *J* = 2.8, H–C(7)); 5.15 (br. *t*, *J* = 7.2, H–C(9)); 4.66 (*d*, *J* = 7.1, H–C(1′)); 3.77 (*d*, *J* = 2.8, H–C(7a)); 4.0–3.6, 3.5–3.4 (2*m*, glucose protons); 2.78 (*dd*, *J* = 15.1, 7.8), 2.61 (*dd*, *J* = 15.1, 6.6, together 2H–C(8)); 1.70, 1.66 (2*s*, 3H–C(11), 3H–C(12)). ^{13}C-NMR ((D$_6$)Acetone): 196.13 (C(2)); 151.30, 150.21 (C(3), C(6)); 135.23 (C(10)); 128.64, 122.75 (C(2a), C(6a)); 121.55, 121.42 (C(4), C(5)); 118.28 (C(9)); 104.09 (C(1′)); 77.74, 77.22 (C(3′), C(5′)); 74.03 (C(2′)); 70.94 (C(4′)); 62.39 (C(6′)); 61.95 (C(1a)); 61.49, 60.53 (C(7), C(7a)); 27.18 (C(8)); 25.77 (C(12)); 17.93 (C(11)). DCI-MS (NH_3, positive ions): 456 ($[M + NH_4]^+$), 439 ($[M + H]^+$), 294 ($[(M + NH_4) - 162]^+$), 277 ($[(M + H) - 162]^+$), 257, 180.

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