HPLC-SPE-NMR analysis of furanosesquiterpenoids from bark exudates of Commiphora swynnertonii Burrt

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from bark exudates of *Commiphora swynnertonii* Burrt.

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Abstract

Bark exudate of the tree *Commiphora swynnertonii* Burtt. (Burseraceae) is used by ethnic groups in Northern Tanzania and Southern Kenya, to treat various diseases in humans and to kill ectoparasites infesting livestock. The acaricidal activity has been demonstrated *in vitro* and *in vivo*. The aim of this study was to isolate the main constituents of the exudate. The exudate was fractionated by Flash Chromatography, purified by HPLC-SPE and subjected to NMR analysis for structural elucidation. Five furanosesquiterpenoids were isolated and identified as 6-oxodendrolasin, (*E*)-6-oxoisodendrolasin, (*Z*)-6-oxoisodendrolasin, crassifolone and 7,8-dihydroisodendrolasin, the latter one being reported here for the first time.

Key words: Commiphora swynnertonii; Furanosesquiterpenoids; 7,8-Dihydroisodendrolasin; LC-SPE-NMR

1. Introduction

Continuing running research lines on medicinal plants from Tanzania (Maregesi et al., 2010), the present investigation focused on the bark exudate of *Commiphora swynnertonii* Burtt. The genus *Commiphora* (Burseraceae) is well known for its ethnomedicinal uses. Shen et al. (2012) reviewed the traditional medicinal uses, phytochemistry and pharmacology of the genus (Shen et al., 2012). The resinous exudates of the most popular species in this genus (including *C. myrrha* (Nees) Engl., *C. gileadensis* (L.) C.Chr. (or *C. opabalsamum* Baill.), *C. mukul* (Hook ex Stocks) Engl. (guggul)*, C. africana* (A.Rich.) Endl. and *C. erythreia* (Ehrenb.) Engl.) have been demonstrated to exhibit anti-inflammatory, anti-microbial and anti-cancer activities (Su et al., 2012). They have been used in the treatment of arthritis, cardiovascular diseases, infections, hyperlipidemia, gynecological diseases and other diseases afflicting livestock. More than 300 compounds have been isolated from this genus (Hanuš et al., 2008). An ethanolic stem bark extract of *C. swynnertonii* possessed *in vitro* as well as *in vivo* antitrypanosomal activity against *Trypanosoma congolense* (Nagagi et al., 2016; Nagagi et al., 2017).

The exudate of *Commiphora swynnertonii* is is used traditionally by ethnic groups in East Africa to treat various diseases in humans and animals (Kalala et al., 2014b). The exudate has been found to have acaricidal activity and tick repellent activity (Kaoneka et al., 2012) (Kalala et al., 2014a; Kaoneka et al., 2007). It has also been demonstrated to have antiviral and antibacterial activity (Bakari et al., 2012; Mkangara et al., 2014). However, there are no reports on chemical constituents of the exudate. The aim of this study was to fractionate the exudate of *C. swynnertonii*, to isolate and to identify its main chemical constituents. For this purpose, high performance liquid chromatography – solid phase extraction – nuclear magnetic resonance (HPLC-SPE-NMR) spectroscopy was used.

2. Experimental

2.1. General experimental procedures

All solvents were purchased from Acros Organics (Geel, Belgium) or from Fisher Scientific (Leicestershire, UK) and were at HPLC grade. All reagents were purchased from Acros Organics or Sigma–Aldrich (St. Louis, MO, USA). RiOS water was prepared by reverse osmosis; water for HPLC was dispensed by a Milli-Q system from Millipore (Bedford, MA, USA) and passed through a 0.22 mm membrane filter. Analytical plates for thin layer chromatography (TLC) were purchased from Merck (Darmstadt, Germany).

Silica gel 60 F254 plates (20 x 20 cm) were used for normal phase (NP) TLC and silica gel 60 RP-18 F254 plates (10 x 20 cm) for reverse phase (RP) TLC. The deuterated solvent CD_3OD (99.8% D) was purchased from Sigma–Aldrich. The spraying reagent *p*-anisaldehyde was prepared by mixing 0.5 mL *p*-anisaldehyde (Sigma-Aldrich) with 10 mL glacial acetic acid, 85 mL methanol and 5 mL sulphuric acid.

Separation by Flash Chromatography was carried out on a Reveleris1 iES system (Grace, Columbia, MD, USA) using the Reveleris1 NavigatorTM software, consisting of a binary pump with four solvent selections, an ultraviolet (UV) and evaporating light scattering detector (ELSD), and a fraction collector. A pre-packed Flash Grace Reveleris silica cartridge (120 g) with a particle size of 40 µm was used.

HPLC-SPE-NMR analysis was carried out using an Agilent 1200 series HPLC instrument with degasser, quaternary pump, automatic injection sampler and an UV/VIS detector (variable wavelength) (Agilent Technologies). Detection was performed at 246 nm. After the detector, water was added (3 mL/min) to the eluent stream with a make-up pump (Knauer K 120, Berlin, Germany), to decrease the organic solvent proportion of the eluent and to promote better retention of the peaks on the SPE cartridges using a Bruker / Spark SPE system, equipped with HySphere Resin General Phase (GP) cartridges (polydivinyl-benzene material with particle size 5–15 µm). Solvent residues were removed by drying the cartridges with nitrogen gas (N_2). By means of a Gilson Liquid Handler 125 the compounds were eluted with deuterated solvent into NMR tubes.

NMR spectra were recorded on a Bruker DRX-400 instrument (Rheinstetten, Germany), operating at 400 MHz for ^{1}H and at 100 MHz for ^{13}C, employing a 3-mm broadband inverse (BBI) probe or a 5-mm dual $^{1}H/^{13}C$ probe using standard Bruker pulse sequences. DEPT-135, DEPT-90 and two- dimensional NMR (COSY, HSQC, HMBC) spectra were recorded (spectra are added as supplementary information). In order to assist structure elucidation, a ^{13}C NMR library was used (NMR Predict version 4.8.57, Modgraph).

High resolution mass spectra were obtained with an ESI Xevo G2-XS QTof spectrometer equipped with with MassLynx version 4.1 software. Full scan data were recorded in ESI+ ionization mode from *m/z* 50 to 1500 and the analyser was set in sensitivity mode (approximate resolution: 22,000 FWHM). The spray voltage was set at +1.0 kV and cone voltage at 40 V; cone gas flow and desolvation gas flow at 50 L/h and 1000 L/h, respectively; and source temperature and desolvation temperature at 120 °C and 550 °C, respectively. Leucine-Encephalin was used as lock mass.

Specific rotation was determined on a Jasco P-2000 polarimeter

2.2. Plant material

The exudate of *C. swynnertonii* was collected from the Simanjiro district (4° 00' 00" S and 36° 30' 00" E), Manyara Region in Tanzania. The tree was identified by a botanist, Mr. John Elia, from the Tanzania National Herbarium in Arusha. The voucher specimen number WK01 was deposited in the National Herbarium. The exudate was used without any modification or pretreatment.

2.3. Extraction and HPLC-SPE-NMR analysis

Five gram of exudate was dissolved in 5 mL dichloromethane, and separated by Flash Chromatography using a solvent gradient progressively evolving from 100% dichloromethane to ethyl acetate/methanol (80/20) + 0.1% formic acid. Fractions were collected based on UV spectroscopic detection at 210 nm and ELSD. Based on the obtained chromatograms and TLC analysis of the obtained fractions, they were pooled together, resulting in 18 fractions. Fractions 9 (yield = 6.7%) , 10 (yield = 7.8%) and 16 (yield = 2.1%) (Fig. 1) were subjected to HPLC-SPE-NMR. A silica-based Apollo C18 (250 x 4.6 mm, 5 µm) (Grace, Columbia, MD, USA) column was used with H_2O + 0.1% formic acid (A) and acetonitrile far UV (B) as the mobile phase. The different compounds were separated using the following gradients: 0 min 44% B – 30 min 52% B – at 32 min 100% B – at 34 min 44%B – stay at 44% B during 6 min (isolation of compound **1** from fraction 9); 0 min 47% B – 30 min 56% B – at 32 min 100% B – at 34 min 44%B – stay at 44% B during 6 min (isolation of compounds **2**, **3** and **4** from fraction 10 and compound **5** from fraction 16). By applying multiple trapping, the same compound was repeatedly trapped on the same cartridge.

*2.3.1. 7,8-Dihydroisodendrolasin ((E)-9-(furan-3-yl)-2,6-dimethylnon-5-en-4-one) (**1**).*

^{1}H- and ^{13}C-NMR: Table 1. HR-MS *m/z* 235.1711 $[M+H]^+$ (calculated for $C_{15}H_{23}O_2$ $[M+H]^+$, 235.1698).

*2.3.2. 6-Oxodendrolasin ((E)-9-(furan-3-yl)-2,6-dimethylnona-2,6-dien-4-one) (**2**).*

^{1}H- and ^{13}C-NMR: Table 1. HR-MS *m/z* 233.1561 $[M+H]^+$ (calculated for $C_{15}H_{21}O_2$ $[M+H]^+$, 233.1542).

*2.3.3. (E)-6-Oxoisodendrolasin ((E)-9-(furan-3-yl)-2,6-dimethylnona-2,5-dien-4-one) (**3**).*

^{1}H- and ^{13}C-NMR: Table 1. HR-MS *m/z* 233.1561 $[M+H]^+$ (calculated for $C_{15}H_{21}O_2$ $[M+H]^+$, 233.1542).

*2.3.4. (Z)-6-Oxoisodendrolasin ((Z)-9-(furan-3-yl)-2,6-dimethylnona-2,5-dien-4-one) (**4**).*

^{1}H- and ^{13}C-NMR: Table 1. HR-MS *m/z* 233.1561 $[M+H]^+$ (calculated for $C_{15}H_{21}O_2$ $[M+H]^+$, 233.1542).

*2.3.5. Crassifolone (4-methyl-1-(7-methyl-4,5,6,7- tetrahydrobenzofuran-7-yl)pent-3-en-2-one) (**5**).* $[\alpha]^{20}_{D}$ –0.98 (c 0.16, MeOH). ^{1}H- and ^{13}C-NMR: Table 1. HR-MS *m/z* 233.1561 $[M+H]^{+}$ (calculated for $C_{15}H_{21}O_2$ $[M+H]^{+}$, calculated 233.1542).

3. Results and Discussion

The ^{1}H-NMR spectrum of compound **2** (Fig. 2) showed 5 signals in the unsaturated region (aromatic or double bond), accounting each for 1 proton, 3 methyl groups appearing each as a singlet, and 3 aliphatic signals integrating each for 2 protons. This information was in agreement with the DEPT-135 and DEPT-90 spectra, in which 3 methylene signals (at 56.1, 29.7 and 25.6 ppm), 3 methyl groups (at 27.7, 20.8 and 16.5 ppm) and 5 unsaturated CH-signals (at 143.8, 140.2, 130.1, 123.9 and 112.0 ppm) were observed. In addition, ^{13}C-NMR showed the presence of an α,β-unsaturated carbonyl moiety at 201.8 ppm, and 3 quaternary unsaturated carbons (at 157.9, 131.3 and 125.9 ppm). 2D-NMR spectroscopy (including COSY, HSQC and HMBC spectra) allowed establishing a furanoid moiety, and a geranoyl-like moiety containing a carbonyl functionality. The presence of 15 carbon atoms suggested this compound to be a sesquiterpene, more in particular a furanosesquiterpene, and comparison with literature data allowed to identify it as 6-oxo-dendrolasin ((*E*)-9-(furan-3-yl)-2,6-dimethylnona-2,6-dien-4-one), isolated before as a stress metabolite of the sweet potato (Burka et al., 1981).

The ^{1}H-NMR spectrum of compound **4** was very similar to those of compound **2**, but the CH_2-signal at 56.1 ppm had disappeared and 3 methylene signals were observed at 34.4, 29.8 and 25.8 ppm, which was in agreement with a -CH_2-CH_2-CH_2- moiety. The signal related to the α,β-unsaturated carbonyl moiety showed increased conjugation, since it had shifted from 201.8 ppm to 193.3 ppm. Both observations indicated that compound **4** was an isomer of compound **2**, in which the double bond had shifted one position. By comparison of the ^{1}H-NMR chemical shifts of the methyl groups with ^{1}H-NMR assignments reported for *(Z)*- and *(E)*-1,6-dioxo-isodendrolasin, compound **4** could be identified as *(Z)*-6-oxoisodendrolasin ((*Z*)-9-(furan-3-yl)-2,6-dimethylnona-2,5-dien-4-one) (Schneider et al., 1984). This compound had been reported before from *Athanasia crithmifolium* and was named *cis*-dihydrophymaspermone (Bohlmann and Rao, 1972). Due to the deshielding effect of the carbonyl group, described by Schneider et al. and the resulting downfield shift of Me-4 (δ_H 2.11) and Me-8 (δ_H 2.12), compound **3** could be identified as *(E)*-6-oxoisodendrolasin ((*E*)-9-(furan-3-yl)-2,6-dimethylnona-2,5-dien-4-one). Also this compound was reported before from the same source and named *trans*-dihydrophymaspermone (Bohlmann and Rao, 1972). In ^{13}C-NMR, the methyl group at C-4 is more shielded

in compound **3** (δ_C 19.3) than in compound **4** (δ_C 25.5), whereas this is the opposite for C-3 (-CH_2-), found at δ_C 41.7 in compound **3** and at δ_C 34.4 in compound **4**.

The ^{1}H- and ^{13}C-NMR spectra of compound **1** again were very similar to those of the previous compounds but could not be related to a compound previously reported. The most striking difference between compound **1** and **2**, **3** and **4** was the occurrence of 2 methyl groups appearing as a doublet at 0.91 ppm in ^{1}H-NMR, indicating that it was the saturated analogue of compound **4** or compound **3**. A direct C-H correlation of H-9/H-10 with δ_C 22.9 (C-9/C-10) was observed in the HSQC experiment. H-9/H-10 and H-8 (δ_H 2.08) were correlated in the ^{1}H-^{1}H COSY spectra, while the HMBC experiment also revealed a long-range C-H correlation between C-8 (δ_C 26.5) and H-9/H-10. Also a long-range C-H correlation between C-7 (δ_C 54.3) and H-8 and a correlation between H-8 and H-7 (δ_H 2.30) were observed in respectively the HMBC and COSY spectrum. The third methyl group appearing at 2.10 ppm in ^{1}H-NMR could be positioned due to several long range C-H correlations present in the HMBC spectrum. C-3 (δ_C 41.5), C-4 (δ_C 160.2) and C-5 (δ_C 124.8) were correlated with this methyl group. A direct C-H correlation of H-3 (δ_H 2.18) with C-3 was observed in the HSQC experiment. H-3 and H-2 (δ_H 1.75) were correlated in the 1H-1H COSY spectrum. Based on the 1D and 2D spectra of the remaining groups and by comparison with published ^{1}H-NMR assignments for *(Z)*- and *(E)*-1,6-dioxo-isodendrolasin (Schneider et al., 1984), compound **1** could be identified as *(E)*-6-oxo-7,8-dihydroisodendrolasin ((*E*)-9-(furan-3-yl)-2,6-dimethylnon-5-en-4-one), reported here for the first time. Compound **1** is an isomer of a constituent numbered as compound 91, reported from roots and aerial parts of *Ursinia abrotanifolia* Spreng., in which the double bond is between C-3 and C-4 (Jakupovic et al., 1992).

Finally the ^{1}H-NMR spectrum of compound **5** showed 3 signals in the unsaturated region (aromatic or double bond), accounting each for 1 proton, 3 methyl groups appearing each as a singlet, and 4 aliphatic multiplets integrating each for 2 protons. This information was in agreement with the DEPT-135 and DEPT-90 spectra, in which 4 methylene signals (at 54.7, 37.4, 23.4 and 21.4 ppm), 3 methyl groups (at 27.7, 27.0 and 20.7 ppm) and 3 unsaturated CH-signals (at 141.5, 126.1 and 111.3 ppm) were observed. In addition, ^{13}C-NMR showed the presence of an α,β-unsaturated carbonyl moiety at 202.7 ppm, 3 quaternary unsaturated carbons (at 156.3, 155.9 and 118.0 ppm), and a quaternary signal at 36.7 ppm. 2D-NMR spectroscopy (including COSY, HSQC and HMBC spectra) allowed to establish a furanoid moiety, an isoprenoid moiety containing a carbonyl functionality, and a -CH_2-CH_2-CH_2- moiety. The presence of 15 carbon atoms suggested this compound to be a sesquiterpene, more in particular a furanosesquiterpene, and comparison with literature data allowed identifying it as crassifolone (4-methyl-1-(7-methyl-4,5,6,7-

tetrahydrobenzofuran-7-yl)pent-3-en-2-one), isolated before from *Myoporum crassifolium* (Menut et al., 2005).

5. Conclusion

The composition of the exu date of *Commipora swynertonii* (Burrt.) was investigated by means of Flash Chromatography and HPLC-SPE-NMR. Four known and one newly reported furanosesquiterpenoids, namely 6-oxodendrolasin, (*E*)-6-oxoisodendrolasin, (*Z*)-6-oxoisodendrolasin, crassifolone and 7,8-dihydroisodendrolasin, were obtained, and were found to constitute a major part of the exudate. In view of the small quantities obtained by HPLC-SPE analysis in this study it was not possible to demonstrate acaricidal or any other bioactivity, yet the isomerization of the compounds after isolation was avoided.

Conflict of interest

The authors declare no conflict of interest.

Acknowledgements

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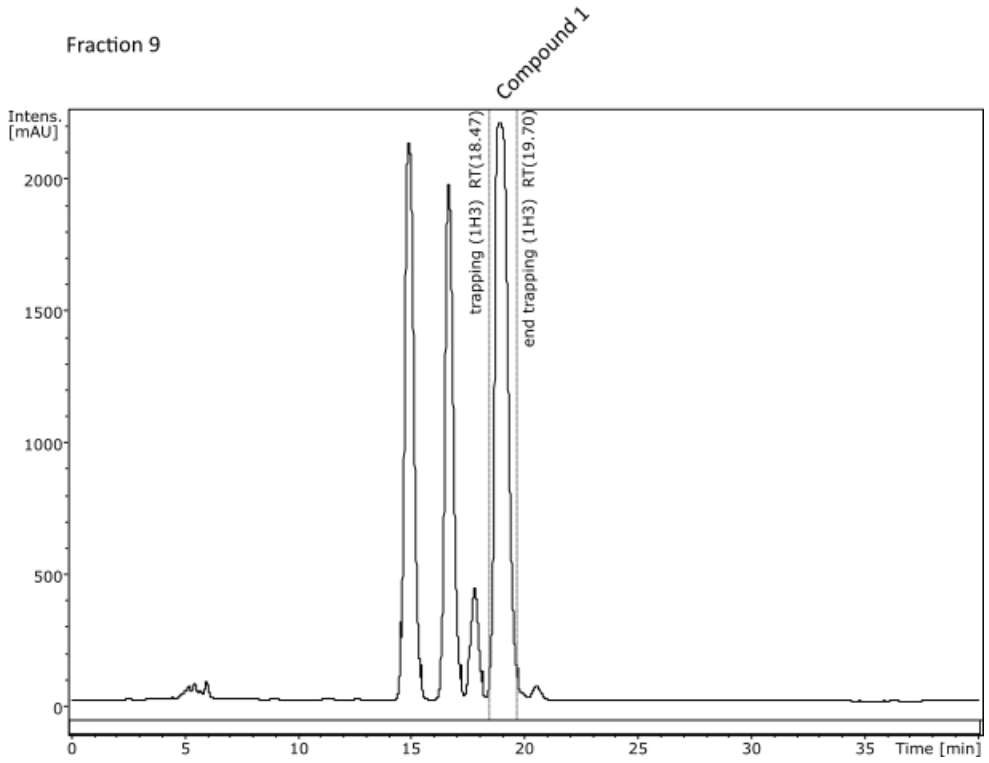
Table 1: ^{1}H and ^{13}C NMR assignments for compound **1 - 5** (δ (ppm)) (CD_3OD) (400 and 100 MHz,respectively)

Carbon no.	**1**$^{+}$		**2**		**3**		**4**		**5**	
	δ_C (ppm)	δ_H (ppm), mult., *J* (Hz)	δ_C (ppm)	δ_H (ppm), mult., *J* (Hz)	δ_C (ppm)	δ_H (ppm), mult., *J* (Hz)	δ_C (ppm)	δ_H (ppm), mult., *J* (Hz)	δ_C (ppm)	δ_H (ppm), mult., *J* (Hz)
1	25.1	2.43, t, 7.5	25.6	2.48, t,7.5	25.2	2.43, t, 7.5	25.8	2.45, t, 7.6	141.5	7.26, d, 1.9
2	29.1	1.75, qu, 7.5	29.7	2.30, q, 7.2	29.2	1.75, qu, 7.7	29.8	1.73, qu, 8.0	111.3	6.14, d, 1.9
3	41.5	2.18, t, 7.5	130.1	5.32, t, 7.1	41.7	2.18, t, 7.4	34.4	2.61, t, 8.0	118.0	
4	160.2		131.3		159.6		160.0		23.4	2.36, m
5	124.8	6.14, d, 1.1	56.1	3.03, s	126.9	6.09, d, 1.1	127.2	6.11, m	21.4	1.74, m
6	203.8		201.8		193.8		193.3		37.4	1.63, m 1.87, m
7	54.3	2.30, d, 7.0	123.9	6.16, m	127.2	6.13, m	127.2	6.11, m	36.7	
8	26.5	2.08, m	157.9		156.4		156.2		155.9	
9	22.9	0.91, dd, 6.6	27.7	1.88, d, 1.1	27.8	1.90, s	27.7	2.12, d, 1.1		
10	22.9	0.91, dd, 6.6	20.8	2.10, d, 1.0	20.8	2.12, s	20.7	1.88, d, 1.2		

4-Me	19.4	2,10, d, 1.1	16.5	1.56	19.3	2.11, d, 0.9	25.5	1.89, d, 1.0		
1’	140.3	7.27, br s	140.2	7.25, br s	140.2	7.27, br s	140.1	7.28, br s	54.7	2.73, d, 13.0
										2.58, d, 13.0
2’	125.8		125.9		125.9		126.1		202.7	
3’	111.8	6.30, br s	112.0	6.30, br s	111.8	6.31, br s	111.9	6.30, br s	126.1	5.84, m
4’	144.1	7.39, br s	143.8	7.36, br s	144.1	7.38, br s	143.9	7.37, br s	156.3	
5’									27.7	1.78, d, 1.16
6’									20.7	2.03, d, 1.1
7’									27.0	1.28, s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Compound 1
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[mAU]
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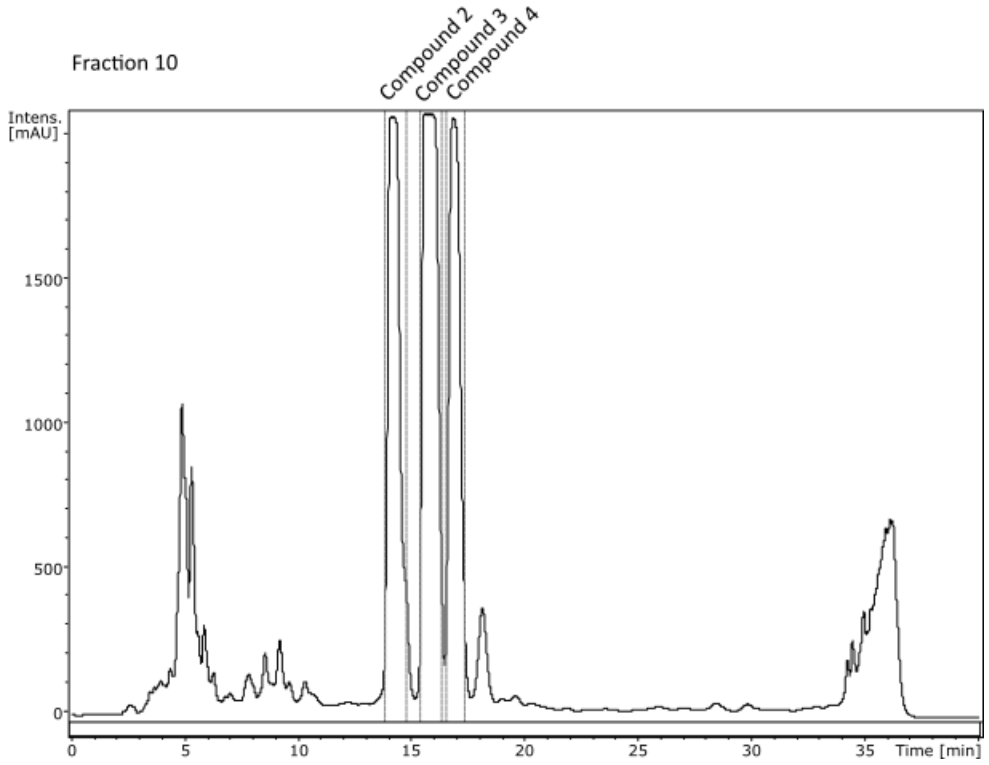
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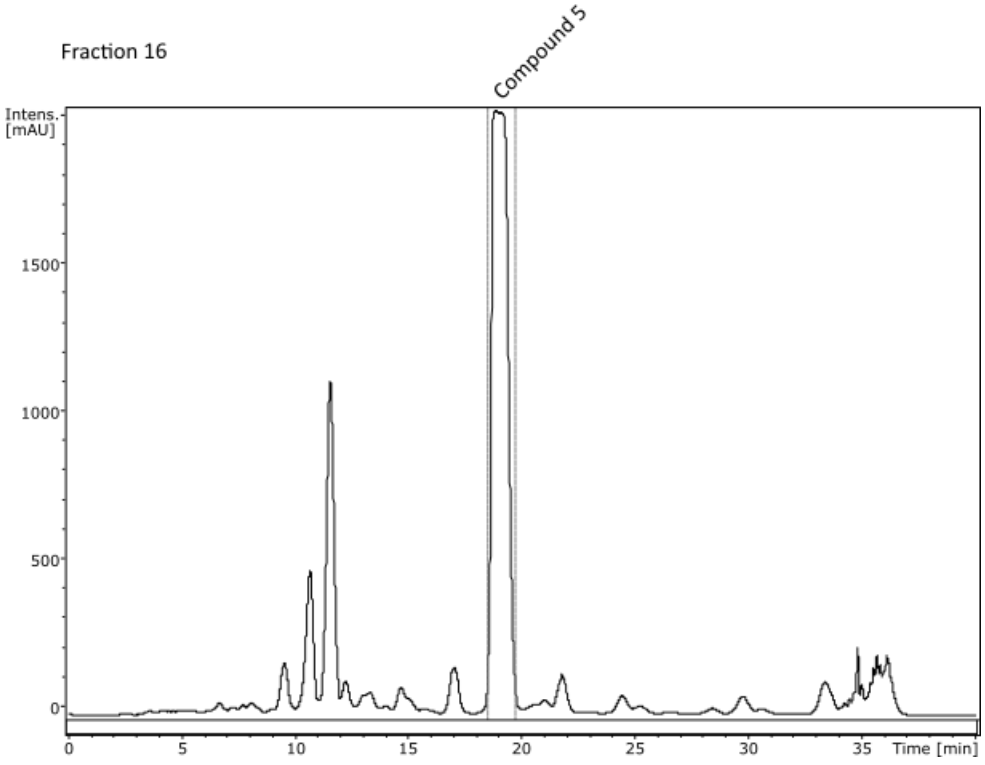

Figure 1: HPLC-UV chromatogram (246 nm) of fraction 9, 10 and 16, obtained by Flash chromatography

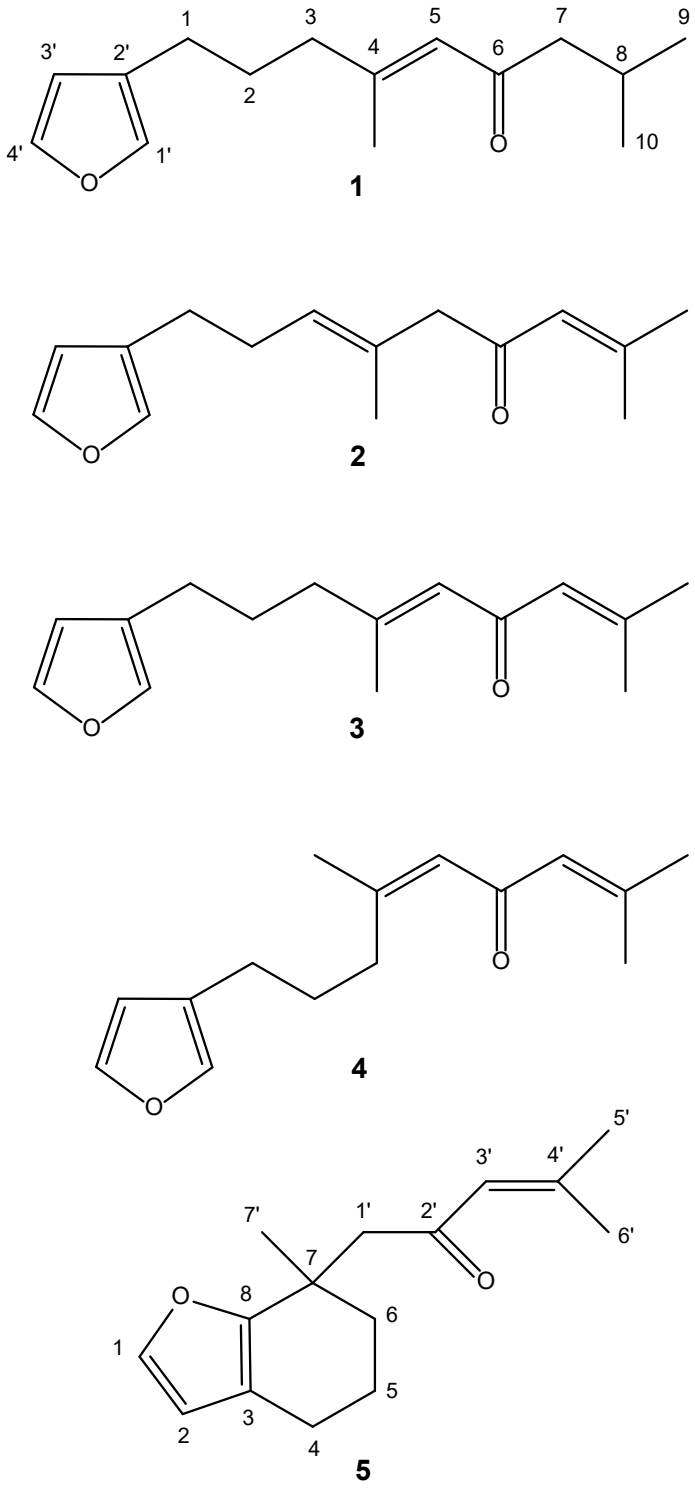

Figure 2: Structure of compound **1** – **5**

Supplementary Information

HPLC-SPE-NMR analysis of furanosesquiterpenoids from bark exudates of *Commiphora swynnertonii* Burrt.

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