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Antifeedant and ovicidal activities of a new cassane and other compounds from *Caesalpinia welwitschiana* Oliv. and *Caesalpinia bonduc* L. against *Tuta absoluta* (Lepidoptera: Gelechiidae)

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ABSTRACT

Methanolic extracts of liana of *Caesalpinia welwitschiana* and leaves *of C. bonduc* were found to possess moderate antifeedant and ovicidal activities against *Tuta absoluta*. Bioassay-guided isolation of constituents from the most active fraction of *C. welwitschiana* led to the identification of four known compounds [isobonducellin **1a** and bonducellin **1 b**, intricatinol **2**, (-)-epigallocatechin-3-*O*-gallate **4**] and one new constituent [welwitschianic acid **3**]. The most active fraction of *C. bonduc* afforded two known constituents neocaesalpin L **5** and neocaesalpin A **6**. The isolated structures were elucidated on the basis of their MS, UV, IR and 1 & 2 D NMR spectra and by comparison with literature data. Compounds **2**, **4**-**6** were showed antifeedant and ovicidal properties against *T. absoluta,* some comparable to that of azadirachtin at 50, 100 and 200 ng/µl. Overall, the present study, conclude that the two species of the plant could be a promising source of eco-friendly botanical constituents.

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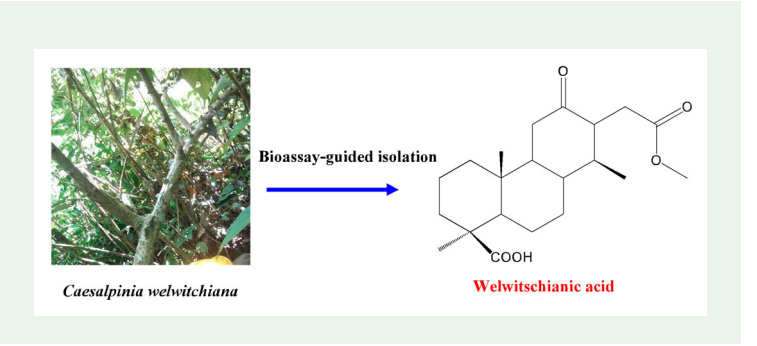

1. Introduction

Tomato (*Lycopersicon esculentum* Mill.), which belongs to the Solanaceae family, is one of the most important vegetables grown all over the world, with 5 million hectares planted worldwide and 170 million tons produced yearly (Biondi et al. 2018). The yields of this delicious crop have been decreasing during the last decade mostly due to the attack of the tomato plants by the tomato pinworm, *Tuta absoluta* Meyrick (Lepidoptera: Gelechiidae) (Campos et al. 2017; Biondi et al. 2018;). This invasive pest is native of South America, and in 2006, it was introduction in Spain. Then, it has spread rapidly throughout Afro-Eurasia and Middle East countries (Sylla et al. 2017; Sankarganesh et al. 2017; Xian 2017; Biondi et al. 2018; Desneux et al. 2010; Seplyarsky et al. 2010). Plants are damaged by direct feeding on leaves, stems, buds, calyces, young fruit, or ripe fruit and by the invasion of secondary pathogens which enter through the wounds made by the pest. It can cause up to 90% loss of yield and fruit quality under greenhouses and field conditions. Presently, the pest also threaten other Solonaceae plants such as eggplant (*Solanum melongena* L.), potato (*Solanum tuberosum* L.), common bean (*Phaseolus vulgaris* L.), and sweet pepper (*Solanum muricatum* L.). It is now considered as a global economic harmful pest to this family plants, particularly to tomato (Desneux et al. 2011; Megido et al. 2013).

Different type of strategies have been implemented to control this pest, including, cultural control measures, and use of natural enemies, resistance varieties of tomato, use of insect's sex pheromone lures and use of synthetic pesticides (Oliveira et al. 2009; Ferracini et al. 2012; Jaworski et al. 2013; Megido et al. 2013; Zappalà et al. 2013; Ingegno et al. 2017). Synthetic chemicals have been the mainly used to control the tomato borer. However, the blanket spraying application of these synthetic compounds has accelerated the evolution of resistance in the pest (Gontijo et al. 2013; Biondi et al. 2018; Roditakis et al. 2018). Furthermore, the indiscriminate applications of the synthetic pesticides are harmful to both man and environment and disrupted-existing integrated pest management (IPM) programs. Green chemistry using bio-pesticide from plant species have been proposed as an alternative method to control agricultural pest (Brunherotto and Vendramim 2001; Ghanim and Ghani 2014; Sannino and Piro 2015; Campolo et al. 2017).The botanical pesticides are, in fact, naturally occurring chemicals extracted from plants having insecticidal activity, often

slow-acting crop protectants that are usually safer to humans and the environment than conventional pesticides and with minimal residual effects (Essoung et al. 2017; 2018; Nagdy and Abdulrahman 2017; Yarou et al. 2018).

Caesalpinia is a genus of flowering plant belonging to the Fabaceae-Caesalpiniaceae family. About 150 species have been found worldwide, with seven growing in Central and East Africa (Bisby et al. 1994). Earlier reports on *C. welwitschiana* and *C. bonduc* extracts and isolated constituents shown that they could be a promising biopesticide plant with antifeedant, larvicidal and pupicidal activities (Baskar et al. 2012, 2018; Essoung et al. 2017). Previous phytochemical studies of some species reported the presence of various classes of secondary metabolites, including flavonoids, cassane type-diterpenoids, cyclohexene, triterpenoids, phenols, steroids and alkaloids (Udenigwe et al. 2007; Xu et al. 2016; Essoung et al. 2017; Baskar et al. 2018). Extracts of some plants and constituents from this genus showed interesting biological effects, such as antimalarial (Linn et al. 2005), insecticidal (Baskar et al. 2012, 2018; Zanin et al. 2012; Essoung et al. 2017) and anticancer (Zheng et al. 2013) activities.

In our search for new insecticide constituents from African medicinal plants, the methanolic extracts of the liana of *C. welwitschiana* and leaves of *C. bonduc* were investigated for the control of *T. absoluta*. Herein, we report on the antifeedant and ovicidal effects of the methanolic extracts of both plants and, bioassay-guided isolation and structure elucidation of active constituents.

2. Results and discussion

In preliminary screening, bioassay-guided fractionations of the methanolic extracts of the liana of *C. welwitschiana* and the leaves of *C. bonduc* showed moderate antifeedant and ovicidal activities on *T. absoluta*. This led us to investigate the compounds responsible for activity and in this line, seven constituents of the extracts were identified (Figure 1).

2.1. Structure determination of compound 1-6

Compound **3** (0.5 mg) was isolated as a colourless amorphous solid. Its molecular formula, $C_{21}H_{32}O_5$, representing six double-bond equivalents, was deduced from the HRESIMS which showed a pseudo-molecular ion peak $[M+H]^+$ at *m/z* 365.3781 (calc. 365.4366 for $C_{21}H_{33}O_5$). The IR spectrum exhibited absorption bands for hydroxyl (3486 cm^{-1}) and carbonyl (1706 cm^{-1}) groups. The ^{13}C NMR spectrum (Table S1, supplementary material) displayed signals for twenty one carbon atoms, which were sorted by HSQC techniques into five quaternary carbons including three carbonyl groups [δ_C 172.3 (COOMe C-16), 178.8 (COOH C-19), and 210.1 (ketone C-12)]; five methine groups at δ_C 29.6 (C-14), 39.8 (C-9), 48.7 (C-5), 49.8 (C-8) and 51.3 (C-13); seven methylene groups; and four methyl groups including one methoxy at δ_C 50.6. The ^1H NMR spectrum (Table S1, supplementary material) exhibited signals of seven methylenes in the range of 1.32-2.72 ppm; five methines [δ_H 3.09 (H-13, m), 2.10 (H-14, m), 2.08 (H-9, m), 1.75 (H-5, m) and 1.52 (H-8, m)], three methyls at δ_H 0.65 (d, $J = 7.0$ Hz, H-17), 1.04 (s, H-20) and 1.21 (s, H-18) and one methoxyl group at δ_H

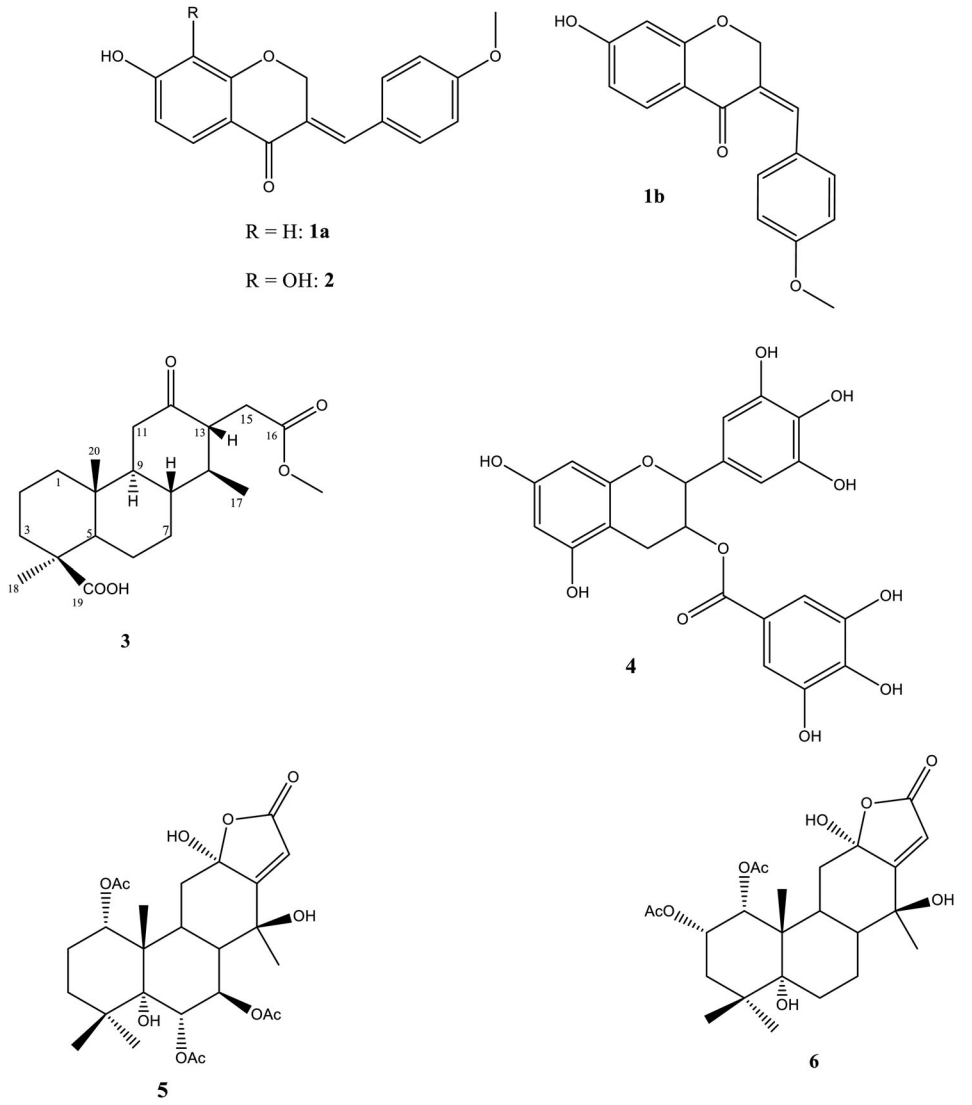

Figure 1. Structures of compounds (**1** -**6**) isolated from the MeOH extract of *Caesalpinia welwitschinia* liana and *Caesalpinia bonduc* leaves.

3.61 (s). The above-mentioned data indicated that compound **3** was a tricyclic cassane-type diterpene with a ketone, carboxylic acid and carbomethoxy groups. The cassane-type diterpene skeleton was in agreement with the COSY experiment (Figure S1a, supplementary material). In fact, analysis of this spectrum showed correlations between H-15/H-13, H-13/H-14, H-14/H-17/H-8, H-8/H-9/H-7, H-9/H-11 and H-5/H-6; which led to the partial structures depicted by the bold lines in Figure 2a. The positions of the substituents were assigned based on the HMBC correlations. The long-range correlations observed on this spectrum (Figure S1a, supplementary material) between the protons H-3 (δ_H 1.77) and H-18 (δ_H 1.21) with the carbonyl at δ_C 178.8 led to the assignment of the acid group at C-19. The position of the carbomethoxy group was determined from the correlations between the methoxy protons at

δ_H 3.61, the methine H-13 (δ_H 3.09) and the methylene H-15 (δ_H 2.15 and 2.72) with the carbonyl group at δ_C 172.3. The ketone was also located at C-12 according to the correlations between the protons H-11, H-14 and H-15 with the carbonyl at δ_C 210.1. The relative configuration of **3** was determined by analysis of coupling constants and NOESY spectrum. The absence of the nuclear Overhauser enhancement (NOE) between H-14 (m), and H-17 ($J = 7.0$ Hz); between H-13 (m) and H-15 (2.72 $J = 16.6$, 8.7 Hz; 2.15 $J = 16.6$, 5.2 Hz) and between H-13 (m) and H-14 (m), suggested that they are oppositely oriented. Therefore, the structure of **3** was assigned as 13-carbomethoxy-12-oxocassa-19β-oic acid, to which a trivial name of welwitschianic acid was given.

The structures of the known constituents were identified by analyses of their ^{1}H and ^{13}C NMR as well as their ESIMS and by comparison with data described in the literature (Table S2). Compound **1** was identified as a mixture of *E* and *Z* geometric isomers, respectively, bonducellin (**1a**) and isoboncellin (**1 b**)(Maheswara et al. 2006). In fact, signals observed on its ^{1}H and ^{13}C NMR spectra at δ_H5.42 (2H, d, $J = 1.9$, H_2-2)/67.8 (C-2), 7.72 (1H, br t, H-9)/135.2 (C-9) are characteristic of *E* isomer and those at 5.03 (2H, br d, H_2-2)/75.5 (C-2), 6.99 (1H, br t, H-9)/139.1 (C-9) for the *Z* isomer (Srinivas et al. 2003). Other compounds were identified as intricatinol (**2**) (Wall et al. 1989), (-)-Epigallocatechin-3-*O*-gallate (**4**) (Zhusupova and Abil'kaeva 2006), Neoceasalpin L (**5**) and Neoceasalpin A (**6**) (Li et al. 2006).

2.2. Biological activities of the isolates

Each of the extract and some of the isolates were evaluated on *T. absoluta* (Figures S2 and S3, supplementary material). All the tested isolates showed low feeding deterrence (<12% at 100 ng/µl) and ovicidal effect (<35% at 100 ng/µl) on *T. absoluta* relative to the crude extracts and the positive control azadirachtin (Figures S2 and S3, supplementary material). For both antifeedant and ovicidal assays, the methanolic extract of the leaves of *C. bonduc* leaves was the most active (49.9% and 53% at 100 ng/µl, respectively). The most antifeedant and ovicidal constituent was Neoceasalpin L (**5**) with 10% and 34% at 100 ng/µl, respectively. The Analysis of Variance (ANOVA) showed significant differences between the tested materials ($F = 16.4$, $DF = 8$, $P < 0.0001$). In all assays, no response was found in the negative control (acetone treatment).

Comparing extracts and isolates, extracts were most active in antifeedant and ovicidal assays than the isolated constituents. This might suggest possible additive or synergic interactions among the constituents, resulting in enhanced activity of the extracts. Generally, insect eggs are the more vulnerable stage to toxic compounds; however, because of their sessile nature, the structure of the eggs protects the developing embryos and may interfere with the penetration of ovicidal compounds (Koppel et al. 2011). Interestingly, Tomé et al. (2012) reported low level of ovicidal effect of pyriproxyfen regulator on *T. absoluta,* but found delayed mortality on the larval stage. Similar observation was made by Campolo et al. (2017), who recorded mortality starting three days after indoxacarb exposure on tomato borer's egg when newly emerged larvae attempted to feed. So, it will be interesting to monitor time-course effects of the individual compounds isolated in the present study, as well as different blends,

over extended periods to see if similar patterns or growth-disrupting activities are also observed.

The study shows that cassane-type diterpenes and flavonoids constituents have significant anti-insect activities. It will be interesting to isolate a series of other cassanes and flavonoids from different *Caesalpinia* species and undertake detailed structure-activity studies on the tomato borer to identify structural features associated with their activities. Apart from their insecticidal activity, some plant extracts and/or their constituents lead to negative impacts on the host plant. Further work is needed to test their efficacy under field conditions. In addition, the effects of different doses of *Caesalpinia* plant extracts on non-target organisms, such as pollinators, natural enemies, and soil dwellings, as well as their phytotoxicity on the target plants, need to be studied.

3. Experimental

3.1. Plant material

The liana *Caesalpinia welwitschiana* Oliv. were collected in November 2014 at Mararaba village, East Cameroon (5° 34′ 55″ N/13° 51′ 33″ E) and the leaves *C. Bonduc* L., at Ebodié beach, Kribi, South Cameroon (2° 34′ 0″ N/9° 50′ 0″ E). The taxonomic identification was performed by Mr Victor Nana, a plant taxonomist at the National Herbarium of Cameroon, where voucher specimens (no. HNC 51336 and HNC 52547, respectively) were deposited.

3.2. Insects

The insects used for bioassays originated from a colony reared at the International Centre of Insect Physiology and Ecology (ICIPE), Duduville Campus, Nairobi, Kenya. The original population from pupae and larvae of *T. absoluta,* was collected in the field in October 2016 from the untreated tomato plants (*Lycopersicon esculentum* Mill.) in Taveta town, Coastal region of Kenya, without any history of exposure to pesticides. The insects collected were initially maintained on tomato plants under quarantine using cage chambers (80 × 80 × 95 cm) to identify any parasitized individuals before the establishment of the colony, which was maintained at 26 ± 2 °C, relative humidity ranging from 60 to 70% and photoperiod of 12 hours.

3.3. Extraction and bioassay-guided isolation of compounds

Air-dried and powdered liana of *C. welwitschiana* (800.6 g) and leaves of *C. bonduc* (402.3 g) were separately extracted with methanol (4 L, 72 h x 3) at room temperature with constant shaking. Extra solvent was removed under reduced pressure at the temperature of 40 °C to yield 21.6 g dark reddish and 26.9 g dark greenish crude extracts, respectively. Masses of 16.6 g and 20.9 g, respectively, of these extracts were subjected to MPLC on silica gel 230-400 mesh (Buchi MPLC, C-601/C-605 dual pump) eluted with mixtures of petroleum ether/EtOAc followed by EtOAc/MeOH. The solvents were of analytical grade (Fisher Chemical Germany Limited, LE11 5RG). Eighty-three and ninety fractions of 125 mL each were collected and grouped into five ($F_{1\text{-}5}$) and four ($F_{A\text{-}D}$)

main fractions, respectively, based on their TLC profiles, which were performed using pre-coated aluminium silica gel 60 F_{254} plates (Merck, 0.25 mm thickness). Spots were visualized under UV light (254 and 365 nm) or using ceric sulphate reagent. All fractions were bio-assayed on *T. absoluta* using the methods described below.

The most active fraction F_4 (6.8 g) of the methanolic extract of the liana of *C. welwitschiana* liana was subjected to column chromatography (2.5 × 40.0 cm) over silica gel 230-400 mesh (Merck) eluted with petroleum ether - EtOAc - MeOH gradient system, resulting in the isolation of the mixture of isomers isobonducellin **1a** and bonducellin **1 b (**0.8 mg). Three sub-fractions F_{4A-C} were obtained and the sub-fraction F_{4-B} (400.4 mg) was re-chromatographed (3.5 × 14.8 cm) using the same solvent system, and afforded intricatinol (**2,** 11.2 mg) and welwitschianic acid (**3**, 0.5 mg). The sub-fraction F_{4-C} (135.7 mg) was also re-chromatographed on a preparative HPLC (Waters K-13APS604M analytic LC equipped with two pumps of K-515, a UV detector 2424, and a Kinetex® 5 μM, C_{18} 100 Å column 250 × 21.2 mm, on a reverse phase silica gel, 40-63 μM, Merck, Darmstadt, Germany), at a flow rate of 2 ml/min, eluted with ACN/H_2O (40: 90) to yield (-)-epigallocatechin-3-*O*-gallate (**4**, 8.3 mg).

The most active fraction F_C (7.1 g) of the leaves of *C. bonduc* leaves was chromatographed on a silica gel column (2.5 × 40.0 cm) using petroleum ether – EtOAc - MeOH gradient system as eluent to give neocaesalpin L (**5,** 7.5 mg) and neocaesalpin A (**6**, 4.1 mg).

All the isolated compounds were identified by analysis of their MS, UV, IR and 1 D& 2 D NMR spectra, and by comparison with reported data. High- and low-resolution electrospray ionization mass spectrometry (ESI-MS) experiments were performed using an Agilent 1100 mass spectrometer (Agilent, USA). Fourier transform infrared (FT-IR) spectra were recorded on Shimadzu IRAffinity-1S. 1 D and 2 D NMR spectra were run on Bruker Ulta Shield™ spectrometers operating at 400 or 500 MHz, with chemical shifts (δ) expressed in ppm with reference to the solvent signals.

13-carbomethoxy-12-oxocassa-19*β*-oic acid (welwitschianic acid) (**3**: 0.5 mg): colourless amorphous powder, IR (KBr): ν_{max} 3,48,62,47,92,16,01,71,00,00,00,000 cm^{-1}; HR-ESI-MS *m/z* 365.3781 (calc. 365.4366 for $C_{21}H_{33}O_5$ $[M+H]^+$); ^1H (500 MHz, Acetone-d_6) δ_H 1.60 (2H, m, H-1), 1.55-1.64 (2H, m, H-2), 1.77 (2H, m, H-3), 1.75 (1H, m, H-5), 1.32-1.58 (2H, m, H-6), 1.40-1.66 (2H, m, H-7), 1.52 (1H, m, H-8), 2.08 (1H, m, H-9), 2.22 (2H, m, H-11), 3.09 (1H, m, H-13), 2.10 (1H, m, H-14), 2.72 (1H, dd, $J = 16.6$, 8.7 Hz, H-15a), 2.15 (1H, dd, $J = 16.6$, 5.2 Hz, H-15b), 0.65 (3H, d, $J = 7.0$ Hz, H-17), 1.21 (3H, s, H-18), 1.04 (3H, s, H-20), 3.61 (3H, s, OCH_3); ^{13}C (125 MHz, Acetone-d_6) δ_C 210.1 (C-12), 178.8 (C-19), 172.31 (C-16), 51.3 (C-13), 50.6 (OCH_3), 49.8 (C-8), 48.7 (C-5), 46.5 (C-4), 40.0 (C-11), 39.9 (C-10), 39.8 (C-9), 36.6 (C-1), 36.5 (C-3), 31.2 (C-15), 30.4 (C-7), 29.6 (C-14), 23.8 (C-6), 17.6 (C-2), 16.3 (C-18), 13.5 (C-20), 8.1 (C-17).

3.4. Biological assays

The antifeedant effects were tested by the conventional leaf disc method against second-instar larvae of *T. absoluta* (Abdelgaleil and Nakatani 2003). Leaf discs (24 mm diameter) of tomato leaves (Variety Moneymaker) were immersed in an acetone solution of the test extract/compounds for 2 s. After solvent evaporation, the treated disc arranged alternatively with another control disc (immersed in acetone only) close

to the wall of a Petri dish. Ten larvae were used for each Petri dish. Four replicates for each concentration were carried out. After 6 hours, the antifeedant effects were calculated from the following equation: % antifeedant = 100 x (C - T/C), where C and T are the weight of control and treatment leaf discs, respectively.

For the assessment of ovicidal property, the method described by Yanar et al. (2011) was used. 10 adult females of *Tuta absoluta* were introduced on detached tomato leaf for oviposition and kept overnight in the petri dish. The leaves were padded with water-soaked cotton. After 24 h, the introduced moths were removed with the help of soft hair brush. The eggs laid on tomato leaves were counted under microscope and leaves with 20 eggs (one-day old) were sprayed with 0.5 ml of each concentrate of the tested material. Five replications for each treatment were done. The viability of eggs was determined for both experimental and control batches of eggs for a period of 8 days after oviposition. Those eggs that did not hatch after this period were treated as non-viable.

In both assays, azadirachtin was used as the positive control, while acetone was used as the negative control. The tested materials in both assays were at concentrations of 50, 100 and 200 ng/µl at 25 ± 2 °C and 75 ± 5% relative humidity, with a photoperiod of 12 hours.

3.5. Data analyses

In the antifeedant assays, for each extract and isolated compounds, weights of control and treated discs consumed were compared using the Wilcoxon pair test (Siegel and Castellan 1988). The ovicidal activity of each tested material was subjected to Analysis of Variance (ANOVA) to evaluate the interaction between the samples and the effect of each tested material. Means were compared by Student-Neuman-Kuel (SNK) Test ($P < 0.05$). The entire analyses were implemented using R 3.3.2 software (R R Core Team 2015).

4. Conclusion

Overall, the present study reports the high antifeedant and ovicidal effects of crude extracts of the liana of *C. welwitschiana* and the leaves of *C. bonduc*, compared to those of their seven constituents including one new cassane. Detailed subtractive assays may shed some light on the possible synergistic effects of the different constituents in the extract (Bekele and Hassanali 2001). This result allows us to consider these crude extracts as potential candidates for downstream use in the control of *T. absoluta* in the field with advantage of cheap and easy to obtain them by farmers.

Data accessibility

The datasets supporting this article have been uploaded as part of the Electronic Supplementary Material.

Disclosure statement

No potential conflict of interest was reported by the author(s).

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