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Chemical constituents from the leaves of *Drypetes gerrardii*

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1. Subject and source

The genus *Drypetes* belongs to the family Euphorbiaceae and constitutes about 160 species, worldwide with many species being found in Africa. *Drypetes gerrardii* J. Hutch (Manyenye–Kikuyu; Ol-durdien–Maasai) is a large tree and one of the many species of the *Drypetes* genus found in Kenya. Other species that are widely distributed in Kenya include *Drypetes natalensis* J. Hutch and *Drypetes aromacia* Pax & Hoffm (Kokwaro, 1976).

The leaves of *D. gerrardii* were collected in Kilifi, Coast province in Kenya, in July 2004 and identified by Simon Mathenge, of Nairobi University, Kenya. A voucher specimen (MM/07/04) is deposited in Nairobi University herbarium, Chiromo Campus.

2. Previous work

There are no reports on phytochemical investigation of *D. gerrardii* J. Hutch.

3. Present study

The dried and powdered leaves (1 kg) of *D. gerrardii* were exhaustively and sequentially extracted with petroleum ether, CH₂Cl₂, EtOAc and MeOH. Each extract was concentrated in vacuo to obtain petroleum ether-, chloroform- and ethyl acetate-soluble fractions, respectively. The petroleum ether and the CH₂Cl₂ crude extracts were combined based on their similarity on the TLC plate. The combined extract (32.6 g) was subjected to column chromatography on silica gel using petroleum ether, petroleum ether–EtOAc, EtOAc–MeOH and finally, pure MeOH as the mobile phase to yield 95 fractions (F_{1–95}). Fractions 15–35 were combined and further separated by silica gel column chromatography eluting with petroleum ether–EtOAc (3:1) to give white cotton needles of friedelin (1, 50 mg) (Patra et al., 1990).

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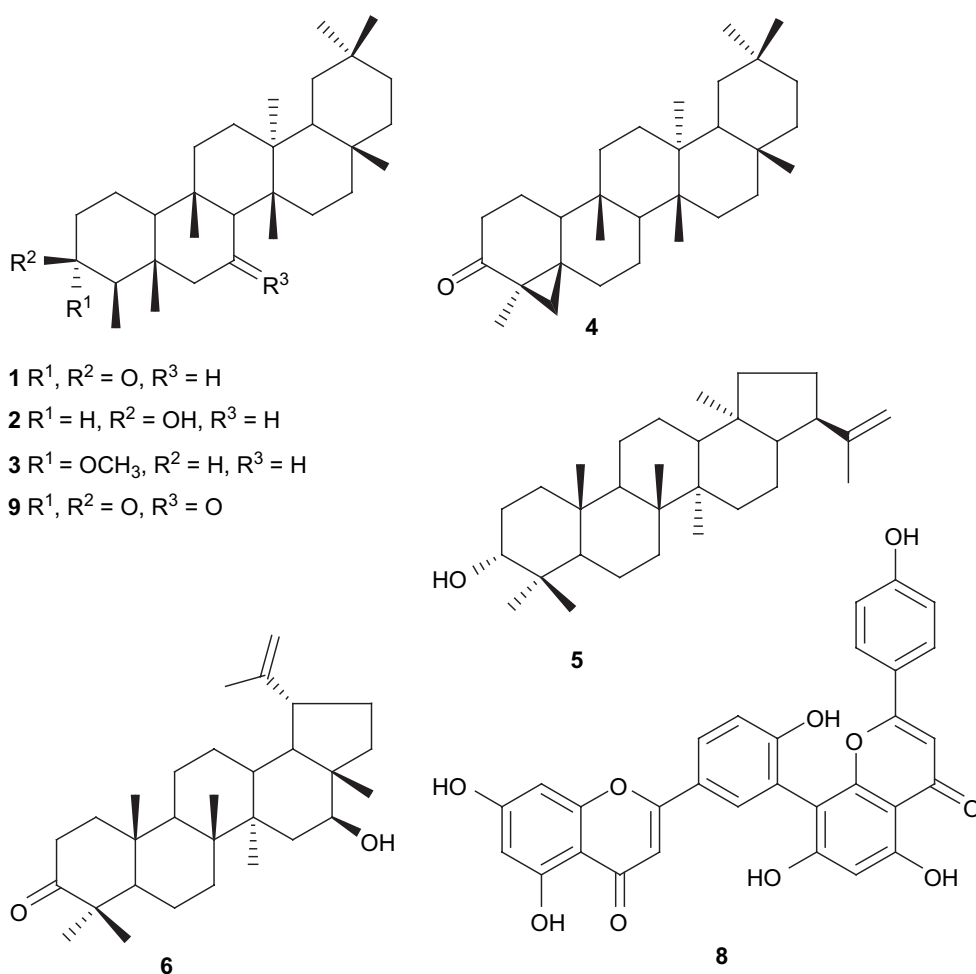
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and epifriedelanol (**2**, 10 mg) (Betancor et al., 1980). Similarly, repeated column chromatography of F_{54–67}, which were eluted with petroleum ether–EtOAc (3:2) furnished friedelanol methyl ether (**3**, 12 mg) (Samaraweera et al., 1983). Further purification of F_{70–75} [petroleum ether–EtOAc (5.5:4.5)] and F_{78–85} [petroleum ether–EtOAc (3:7)] on a Sephadex[®] LH-20 column with CH₂Cl₂–MeOH (7:3) as eluant combined with repeated crystallization using acetone afforded 5 β ,24-cyclofriedelan-3-one (**4**, 8.6 mg) (Connolly et al., 1986).

The crude ethyl acetate extract (15 g) was similarly chromatographed on a silica gel column and eluted with a gradient of petroleum ether, CH₂Cl₂, EtOAc, and MeOH yielding 65 fractions (F_{1–65}). Repeated column chromatography of F_{20–30} using a 5% stepwise gradient of petroleum ether and ethyl acetate afforded 3-epimoretenol (**5**, 6.5 mg) (Khastgir et al., 1967). Similarly repeated CC of fraction F_{31–35}, eluted with a mixture of petroleum ether–EtOAc (8:2) and further purification in a Sephadex column using CH₂Cl₂–MeOH (1:1) gave resinone (**6**, 4.0 mg) (Pyrek and Baranowska, 1977). Fraction F_{38–45} on CC using CH₂Cl₂–EtOAc (4:6), gave β -sitosterol glucopyranoside (**7**, 50 mg) (Seo et al., 1978). Preparative TLC of F_{50–58} eluted with ethyl acetate–MeOH (9.5:0.5) from the column, using CH₂Cl₂–MeOH (7:3) as the solvent system yielded five fractions. The polar fraction was further purified on a Sephadex LH-20 column using CH₂Cl₂–MeOH (1:1) and furnished amentoflavone (**8**, 6 mg) as a yellow powder (Goh et al., 1992; Lin et al., 2001) and friedelane-3,7-dione (**9**, 3.5 mg) (Patra et al., 1990). The structures were established conclusively by UV, IR, MS and extensive ¹H and ¹³C NMR spectra analysis and comparison with data from the literature cited above.

4. Chemotaxonomic significance

The present study reports the isolation of five friedelane-type triterpenoids (**1–4**, **9**), one hopane-type triterpenoid (**5**), one lupane-type triterpenoid (**6**), one steroid (**7**), and one flavone dimer (**8**) for the first time from the leaves of



Scheme 1. Compounds **1–8** isolated from *Drypetes gerrardii*.

D. gerrardii. The occurrence of friedelane-type triterpenoids (**1–3, 9**) in *D. gerrardii* is in agreement with triterpenoid constitution previously reported in other species of *Drypetes* (Dupont et al., 1997; Lin et al., 2001; Ngouela et al., 2003; Wandjia et al., 2000, 2003; Wansi et al., 2006). Thus, the isolation of triterpenoids **1–3, 9** from *Drypetes* species indicates that these compounds could be chemotaxonomic markers for the *Drypetes* genus.

Interestingly, 5 β ,24-cyclofriedelan-3-one (**4**), 3-epimoretenol (**5**) and resinone (**6**) were characterized for the first time from the genus *Drypetes*. Therefore, compounds **4–6** might be useful taxonomic markers for the genus, and thus a contribution to chemotaxonomic studies of the spurge (Euphorbiaceae) family. On the other hand, amentoflavone (**8**) has been reported from *Drypetes littoralis* (Lin et al., 2001) and this is the only record of flavones in a *Drypetes* species, despite their widespread occurrence in the Euphorbiaceae family (Scheme 1).

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