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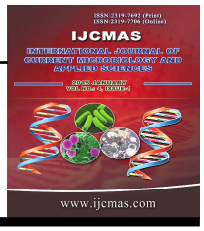

Original Research Article

Phytochemical investigation of *Securidaca longipedunculata* (Polygalaceae) and structure elucidation of benzyl 2-hydroxy-5-methoxy benzoate

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K e y w o r d s

Securidaca longipedunculata, benzyl 2-hydroxy-5-methoxy benzoate,

A B S T R A C T

The plant *Securidaca longipedunculata* (Polygalaceae) is a widely used medicinal plant in most of the African countries. The Phytochemical investigation furnished a liquid compound that was characterized as benzyl 2-hydroxy-5-methoxy benzoate by spectral analysis (IR, ^{1}H-NMR, ^{13}C-NMR and MS).

Introduction

Securidaca longipedunculata Fresen (family: Polygalaceae) is a semi-deciduous shrub or small tree that grows up to 12 meter (36 feet) tall. It is a widely used medicinal plant in most of the African countries such as Angola, Benin, Botswana, Burundi, Cameroon, Chad, Cote d'lvoire, Democratic Republic of Congo, Eritrea, Ethiopia, Gambia, Ghana, Guinea, Kenya, Malawi, Mali, Mozambique, Namibia, Niger, Nigeria, Rwanda, Senegal, Sierra Leone, South Africa, Sudan, Tanzania, Uganda, Zambia and Zimbabwe. The tree also grows in other countries like Cuba, Malaysia and many Asian countries. In Ethiopia it is known as 'Es a manahi' (Amharic name), 'shotora' (Tigrigna name). The common English names are: violet tree, fiber tree and Rhodesian violet.

The flowers are in abundance at the beginning of rainy season, sweetly scented, bright purple or violet racemes and the fruit is winged. Fruit is more or less a round nut, somewhat heavily veined occasionally smooth, bearing a single, oblong, rather curved, membranous wing up to 4 cm long; purplish-green when young, becoming pale, straw-colored when mature. It is a beautiful flowering tree with potential as an ornamental in parks, gardens and along the road sides.

Fruits often hang on the trees for many months and those that stay the longest are said to germinate best. The young leaves are eaten as a vegetable and in sauces. The flowers are suitable for honey production. In Eritrea, this tree is one of the most valuable

low land honey sources. The timber is resistant to termites and decays and used for poles and hut construction. The flowers yield oil and used for some purposes. Bark, roots and seeds are used in arrow poison and root as a snake repellent. Roots are 100% effective as a molluscicide. Due to the presence of saponins, the bark, root bark and crushed seeds give a soapy solution in water and are used as soap for washing clothes.

In Northern Nigeria, it is called "Uwar Magunguna" in Hausa language, literally translated "the mother of all drugs", a tribute to its very numerous medicinal uses (Dapar *et al.,* 2007). In Tanzania, the plant is known as 'Mlyangabako' among the Hehe people in Iringa and Masukemengi" and Zigua people of Tanga. In Iringa, it is used for the management of some manifestation of non-insulin dependent diabetes. A decoction of the dried bark is used to treat bacterial infection and inflammation (Arnold and Gulumian, 1984; De Tommasi *et al.,* 1993) insanity and epilepsy (Mathias, 1982).

The leaves are used for treating wounds, sores, cough, venereal diseases, snake bite and as a purgative (Chhabra *et al.,* 1991; Hedberg, 1983) to treat tuberculosis (Akah and Nwambie,1994; Asres *et al.,* 2001) bilharzias (Kamwendo *et al.,* 1985), skin diseases (Odebiyi, 1978), convulsion in children (Sofowora, 1980). The decoction of the root is used to hasten (accelerate) labour (Kokwaro, 1976; Yu, 1982), to treat malaria (Chhabra *et al.,* 1991), rheumatism (Kloos, 1978) gonorrhea, palpitations, pneumonia, syphilis (Desta, 1993) and asthma (Akah, 1997).

In many parts of Africa, the plant is employed in traditional medicine principally for its psychotropic properties; the aqueous extract of the root is used as psychopharmacological agents (Winkleman and Dobkin de Rios, 1989). They also reported the presence of ergot alkaloid in the extract. The plant has been employed for various rheumatic and inflammatory diseases and as anti-helmintic or purgative agents (Neuwinger, 1996). The use of the plant against snakebites, fish poisoning and in different diseases have been documented (Odebiyi, 1978; Neuwinger, 1996; Burkill, 1997; Oladije *et al.,* 1998). Its use in bacterial and malarial chemotherapy has also been investigated (Akinniyi *et al.,* 1996; Msonthi, 1986). The anti-inflammatory activity of the methanol extract of this plant was reported (Okoli *et al.,* 2005).

In course of our investigation on the root bark of the plant *Securidaca longipedunculata*, an African medicinal plant we isolated a liquid compound whose structure has been fully characterized as Benzyl 2-hydroxy-5-methoxy benzoate (Figure 1) on the basis of spectral analysis. This compound was previously reported by some other workers (Kodpinid *et al.,* 1984) isolated from the root of another plant, *Uvara purpurea* collected from Kroab Island, Patalung province, Thailand and the structure of which was not properly characterized.

There was some ambiguity left behind regarding the location of the methoxyl (OCH_3) group at C-5, its position was not adequately ascertained, more information were necessary to fix its position. Now, we bring more additional information and rational arguments in the analysis of ^{1}H-NMR spectrum that fixes the position of the methoxyl group at C-5 without any doubt.

In earlier experiment the ^{1}H-NMR spectrum was run in CCl_4 using 60 MHz instrument having TMS as an internal standard. In our analysis, the spectrum was run in $CDCl_3$ having TMS using 400 MHz instrument. All

the values (chemical shifts) of the compound shifted to lower field by about δ 0.20 and the spectrum gave a better resolution as regards to splitting pattern of the aromatic protons and that made the analysis simpler for locating the position of the OCH_3 group at C-5.

The signal at 6.45 (1H, d, 8.5 Hz) was due to H-3 proton and signal at 6.64 (1H, d, 8.5 Hz) was due to H-4 proton. The clear ortho coupling with J = 8.5 Hz between H-3 and H-4 clearly locates the position of methoxyl group at C-5. The H-6 proton appeared as a singlet at δ 7.35. The meta coupling between H-4 and H-6 and para coupling between H-3 and H-6 were very weak and became invisible and as a result of which the H-6 proton appeared as undisturbed and clean singlet at δ 7.35.

If the OCH_3 group was present at C-6, the ortho coupling between H-3 and H-4 would not become so clear and perturbed by H-5 proton. All these protons would have appeared as multiplets. Furthermore, the ^{13}C- NMR spectrum has been incorporated as additional information which was not included before in the previous work. The complete analysis of ^{1}H and ^{13}C-NMR spectra are summarized in Table 1.

Experimental

Plant collection and separation of root bark from root

The plant was collected from a place close to Ajora falls (SNNPR), Kambeta Tembaro Zone, Hadero Tunto Zuria Woreda, Ethiopia. The falls is located at an altitude of 1447 meter (approximately 4340 feet) and 300 km away from the capital city Addis Ababa in Ethiopia. It was authenticated by the taxonomist, Dr. Melesse Maryo, National Herbarium, Addis Ababa University, Addis Ababa, Ethiopia (voucher number MM148/2003). After collection, the root was thoroughly washed with water to remove any dust particles. The bark was separated from the root and finally air dried under shade. The air dried bark was then ground with a metal grinder.

Phytochemical investigation of the root bark

The powdered root bark (65g) was first extracted (Soxhlet) with petroleum ether (b.p.60-80^{0}C) for 6 hours. After extraction the plant material was taken out from the chamber and dried in air to remove all the solvents. The dried material was again extracted (Soxhlet) with acetone for 6 hours.

The solvent (acetone) of the extract in the flask was removed in water bath to give a liquid mass (1.17 g, 1.8% yields). This material (acetone extract) was subjected to column chromatography over a column of silica gel (25 g) and elution with different solvent systems furnished a liquid compound (42 mg, 0.065% yield). It showed a single spot on TLC (R_f = 0.5, precoated silica gel on Al-foil, solvent: Petroleum ether: Acetone = 4:1, Iodine vapor). The compound furnished the following spectral analysis.

IR (KBr, cm^{-1}): 1732 (ester), 1652 (αβ-ester), 1583 (aromatic), 1462, 1257 and 1234, 1030 (OCH_3).

^{1}H-NMR (400 MHz, $CDCl_3$,TMS, δ): 3.90 (3H, s, OCH_3), 5.45 (2H, s, -O-CH_2-Ph), 6.45 (1H, H-3, d, J = 8.5 Hz, ortho coupling with H-4), 6.64 (1H, H-4, d, J = 8.5 Hz, ortho coupling with H-3), 7.35 (1H, s, H-6), 7.37 (1H, H-4′, d, J = 8 Hz, ortho coupling with H-3′/ H-5′), 7.43 (1H, H-3′/ H-5′, t, J=8 Hz, ortho coupling with H-2′/ H-6′ and H-4′), 7.51 (1H, H-2′/ H-6′, d, J=8 Hz, ortho coupling with H-3′/ H-5′), 11.50 (1H,

phenolic OH, D_2O exchangeable).

^{13}C-NMR($CDCl_3$, δ): 56.15 (OCH_3), 66.87 (CH_2), 102.38 (CH, C-3), 103.21 (QC, C-1′), 110.06 (CH, C-4), 127.50 (CH, C-6), 128.07 (CH, C-4′), 128.54 (CH, C-3′/C-5′), 135.28 (CH, C-2′/C-6′), 135.79 (QC, C-5), 161.11 (QC, C-2), 163.65 (QC, C-1), 170.94 (CO, ester).

DEPT spectrum showed the presence of 1methoxyl (OCH_3), 1CH_2, 8CH, 5QC, resulting total 15 carbon atoms with a molecular formula $C_{15}H_{14}O_4$.

MS: 281.29 $(M + Na)^+$ for $C_{15}H_{14}O_4$ (MW 258).

On the basis of the above spectral analysis the compound was characterized as Benzyl 2-hydroxy-5-methoxy benzoate (Figure 1).

Result and Discussion

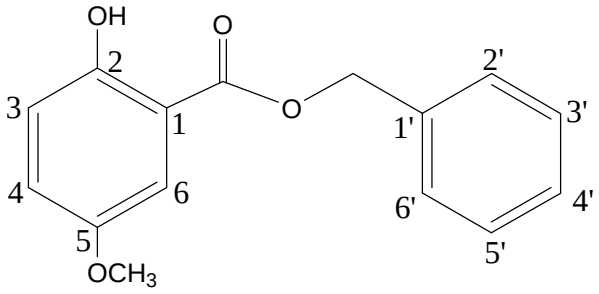
The isolation of benzyl 2-hydroxy-6-methoxy benzoate was earlier reported (Kodpinid *et al.,* 1984) from another plant but the structure was not well characterized. Now, we bring more additional information and rational arguments in the analysis of ^{1}H-NMR spectrum that fixes the position of the methoxyl group at C-5 without any doubt. Furthermore, the ^{13}C- NMR spectrum has been incorporated as additional information which was not included before in the previous work. This is the first report for the isolation of benzyl 2-hydroxy-5-methoxy benzoate from *Securidaca longipedunculata* Fresen.

Table.1 Analysis of 1H and 13C-NMR spectra of Benzyl 2-hydroxy-5-methoxy benzoate

Present findings				**Previous findings**	
^{1}H-NMR	**δ in $CDCl_3$**	**^{13}C-NMR**	**δ in $CDCl_3$**	**^{1}H-NMR**	**δ in CCl_4**
H-1 (QC)	----------	C-1, QC	163.65	H-1 (QC)	--------
H-2 (QC)	----------	C-2, QC	161.11	H-2 (QC)	--------
H-3 (CH)	6.45,1H,d,8.5 Hz	C-3,CH	102.38	H-3 (CH)	6.66 -7.40, 1H, m
H-4 (CH)	6.64,1H,d,8.5 Hz	C-4, CH	110.06	H-4 (CH)	6.66 -7.40, 1H, m
H-5 (QC)	---------	C-5, QC	135.79	H-5 (QC)	---------
H-6 (CH)	7.35,1H, s	C-6, CH	127.50	H-6 (CH)	6.66 -7.40, 1H, m
OCH_3	3.90, 3H, s	OCH_3	56.15	OCH_3	3.67, 3H, s
CH_2	5.45, 2H, s	CH_2	66.87	CH_2	5.26, 2H, s
OH	11.50, 1H, s, D_2O	------	------	OH	10.18, 1H, s, D_2O
-------	--------	CO, QC	170.94	--------	---------
H-1′ (QC)	--------	C-1′, QC	103.21	H-1′ (QC)	--------
H-2′,6′ (CH)	7.51, d, 8 Hz	C-2′,6′, CH	135.28	H-2′,6′ (CH)	7.30, 2H, s
H-3′,5′ (CH)	7.43, d, 8 Hz	C-3′,5′, CH	128.54	H-3′,5′ (CH)	7.30, 2H, s
H-4′ (CH)	7.37, d, 8 Hz	C-4′,CH	128.07	H-4′ (CH)	7.30, 1H, s

Note: 13C-NMR was not reported in the previous literature

Figure.1 Benzyl 2-hydroxy-5-methoxy benzoate



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