NEW DITERPENES FROM BLACKCURRANT BUDS (*RIBES NIGRUM* L.)

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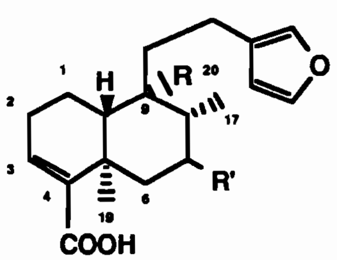
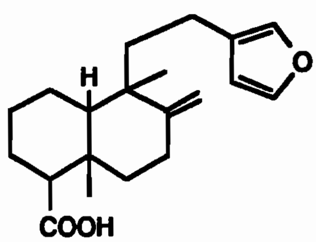
Blackcurrant buds are grown for their characteristic solvent extract, which is highly valued as a flavour enhancer in food products. It has a strong terpenic character dominated by an intense 'catty' note, attributable to the presence of up to 200ppm of 4-methoxy-2-methyl-2-butanethiol (1) in the Tasmanian product. The extract also contains a complex mixture of monoterpenes (10-20%) and sesquiterpenes (5-10%) (mainly hydrocarbons) which have been studied in detail by several groups (2). However the minor oxygenated components (e.g. spathulenol and caryophyllene oxide with conifer-like odours, and linalool and citronellol having floral notes) give the extract its characteristic impact (2).





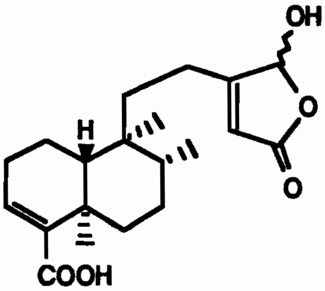
(I) R = CH_3, R' = H, (-)-Hardwickiic acid (VI)

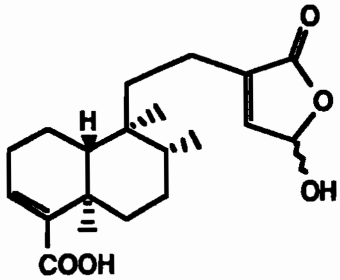
(II) R = CHO, R' = H

(III) R = COOH, R' = H

(IV) R = CH_2OH, R' = H

(V) R = CH_3, R' = CHO





(VII) (VIII)

The high proportion of crystalline diterpene acids (35-50%) in the extract has been recognised for some time but a detailed study of these had not been carried out. In studying French blackcurrant bud extract, Fellous *et. al.* (3) identified (+)-hardwickiic acid ($[\alpha]_D = 123^o$) as the major acid, identical with (+)-hardwickiic acid isolated from *Copaifera officinalis* (4). More recently, Derbesy *et al.* (5) confirmed the presence of hardwickiic acid (34%) and isolated another acid (V) (11%). However, they did not specify the absolute configurations of either of these compounds. Compound (V) is unusual in that it has 21 carbons and although several such compounds are known, they are rare.

In contrast to the findings of Fellous *et. al.* (3), Tasmanian blackcurrant bud extracts have been shown to contain the *laevorotatory* isomer (-)-hardwickiic acid (I, $[\alpha]_D = -131^o$, 29.7%) which also occurs in *Hardwickia pinnata* (6). In addition, a series of three previously unreported compounds has been isolated by a combination of normal phase silica gel column chromatography and reverse-phase HPLC. Three of these are derivatives of (-)-hardwickiic acid oxygenated at the methyl group attached to C9. The aldehyde (II, 3.5%) is a major component with the diacid (III, 0.1%) and hydroxyacid (IV, 0.7%) occurring in small amounts. The structures were determined by a combination of ^1H and ^{13}C nmr techniques and some of the salient features are presented below:

Compound	dC17	dC19	dC20	dH17	dH19	dH20
Hardwickiic acid (I)	15.94	20.57	18.25	0.83(d)	1.26(s)	0.76(s)
Aldehyde (II)	16.70	21.06	206.43	1.09(d)	1.16(s)	9.99(s)
Diacid (III)	16.50	17.98	182.91	1.16(d)	1.25(s)	-
Hydroxyacid (IV)	17.03	20.05	65.47	0.93(d)	1.32(s)	3.77(s)
(VI) Methyl ester				4.58,4.87	1.14(s)	0.71(s)

The other major acidic component is the 8-exo-methylene acid (VI, 3.2%), identified spectroscopically by its similarity with lambertianic acid (7) and compounds (I)-(IV). The proportion of this acid is quite variable and seems particularly useful in distinguishing between certain blackcurrant cultivars.

Two isomeric γ-hydroxybutenolides (VII) and (VIII) were also present in minor amounts as pairs of diastereomers separable by HPLC. They were identified by comparison of nmr spectra with those of similar compounds described in the literature (7). Minor amounts of analogous compounds derived from aldehyde (II) were also isolated by HPLC. These compounds presumably arise from oxidation (8) of the furan ring of (I) and (II), which may be photochemically assisted. Interestingly, no trace of compound (V) was detected despite exhaustive investigation of the acidic fraction of the extract.

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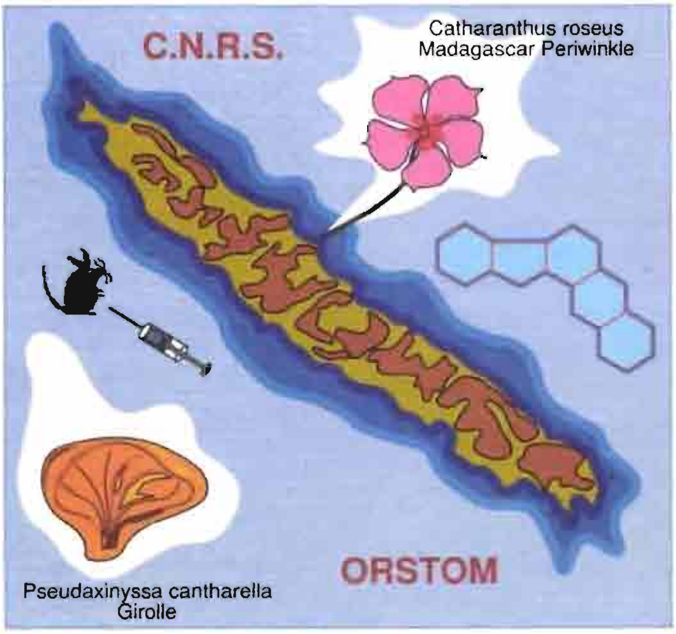

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