quinone from dopamine, even in those regions of the cuticle where ring oxidation of the sclerotizing agent occurs. The resulting black pigment eventually obscures the tan color of N-acetyl dopamine quinone. These reactions are especially evident in weak alleles of ebony where normally tan areas of the cuticle clearly show both tan and black pigmentation.

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SPECIALIA

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Antidesmanol – a new pentacyclic triterpenoid from *Antidesma menasu* Miq. ex. Tul.[1]

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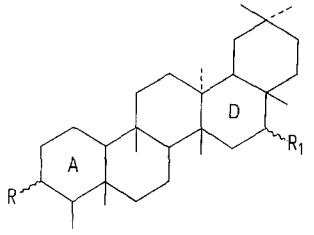
Summary. Antidesmanol (**1**), a new pentacyclic triterpenoid, has been isolated along with n-tritriacontane, friedelin, canophyllal and canophyllol from the aerial parts of *Antidesma menasu*. Based on chemical and spectroscopic evidence, its structure has been established as 3-keto-16α-hydroxyfriedelane. n-Tritriacontane and friedelin have shown antiinflammatory and diuretic activities respectively in experimental animals.

In a preliminary biological screening the petroleum ether extract of the aerial parts of *Antidesma menasu* Miq. ex. Tul. (Euphorbiaceae) showed antiinflammatory and diuretic activities. This prompted us to undertake its detailed chemical investigation. The column chromatography of this material on silica gel yielded n-tritriacontane (0.2% yield), friedelin (0.07%), canophyllal, canophyllol, and a new pentacyclic triterpene (0.044%) designated as antidesmanol (**1**). The present communication deals with the elucidation of the structure of **1** as 3-keto-16α-hydroxyfriedelane.

Antidesmanol (**1**), m.p. 277–280 °C ($CHCl_3$–MeOH); $C_{30}H_{50}O_2$; M^+ 442; $[\alpha]_D^{18°}$ −57° (c, 1, $CHCl_3$); ν_{max}^{KBr} 3400 (OH) and 1720 cm^{-1} (C=O) gave a benzoate (**2**), m.p. 90–91 °C; M^+ 546 $[\alpha]_D^{18°}$ −58.2° ($CHCl_3$). The chemical shift in PMR-spectrum (60 MHz; $CDCl_3$) of the hydroxymethine in antidesmanol acetate (**3**), m.p. 230–232 °C; $C_{32}H_{52}O_3$; M^+ 484; $[\alpha]_D^{18°}$ −38.5° ($CHCl_3$), revealed the secondary nature of the −OH function. The presence of signals for 7 tertiary (δ 0.7–1.18), 1 secondary (δ 1.30) methyl groups and 1 hydroxymethine (δ 3.65) in the PMR-spectrum of **1** coupled with a negative tetranitromethane test suggested it to be a derivative of friedelane group.

Careful examination of the various fragment ions[2–4] (m/e 193, 221, 273, 302, 357 and 371) present in its EI mass spectrum permitted the placement of the carbonyl and



	R	R_1
(1)	=O	α-OH, β-H
(2)	=O	α-OAc, β-H
(3)	=O	α-OBz, β-H
(4)	=O	=O
(5)	α-OH, β-H	α-OH, β-H
(6)	α-H, β-OH	α-OH, β-H
(7)	=O	α-H, β-OH

hydroxy functions at C-3 and in ring D respectively. Oxidation of **1** with Corey's reagent[5] gave a diketone, m.p. 298–299 °C; $C_{30}H_{48}O_2$; M^+ 440; $[\alpha]_D^{18°}$ −35° ($CHCl_3$) identical with the synthetic dione (**4**) prepared earlier by Kikuchi et al.[6], and thus the hydroxy group was fixed at C-16. Evidence for its α-orientation was obtained by the reduction of **1** with Na/isoamyl alcohol to diol **5**, m.p. 288–290 °C; $C_{30}H_{52}O_2$; M^+ 444; $[\alpha]_D^{18°}$ −4.4° ($CHCl_3$), which was found to be identical with the one obtained by the reduction of diketone **4** under similar conditions. On the other hand, the observed dissimilarity between the diols **5** and **6**, [m.p. 275–277 °C; $C_{30}H_{52}O_2$; M^+ 444; $[\alpha]_D^{18°}$ −3° ($CHCl_3$), obtained by $NaBH_4$ reduction of (**1**)] is in conformity with the above stereochemical assignment and therefore the structure **1** is the complete representation of antidesmanol which is a C-16 epimer of pachysonol (**7**) isolated earlier from *Pachysandra terminalis*[6] (Buxaceae).

The antiinflammatory activity of the compounds was tested in mice against carrageenin-induced acute oedema[7]. Out of all compounds tested only n-tritriacontane at 100 mg/kg (p.o.) exhibited 50.6% activity. The diuretic activity was tested in rats[8] and only friedelin at 64 mg/kg (p.o.) showed 99% activity compared with chlorothiazide (125 mg/kg).

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Inhibition of nitrosamine formation by ascorbic acid: participation of free radicals in its anaerobic reaction with nitrite

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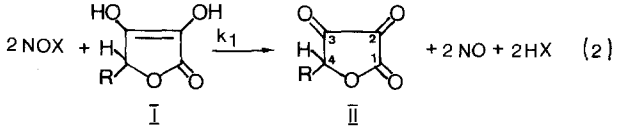
Summary. The participation of semiquinone free radicals during the reaction of ascorbic acid with acidified sodium nitrite has been demonstrated by ESR spectroscopy unambiguously for the first time. Scavenging of the nitrosating agent, reflected by the observed free radical concentration, unexpectedly occurs with scarcely varying efficiency over the pH range 0.1–4.5.

Nitrosamines (NOAs), among the most potent carcinogens currently recognised, are known to form intragastrically following the intake of nitrite together with various primary[1], secondary[2] or tertiary amines[3] (reaction 1).

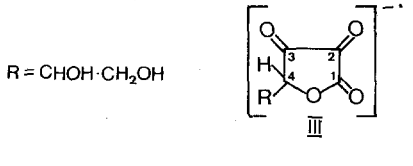
$$NOX + R_1R_2NH \rightarrow R_1R_2N{-}NO + HX \qquad (1)$$

Precursors of NOAs may occur in the human diet, originating form natural and man-made sources[4–7]. It is also known that naturally occurring phenolic substances in foodstuffs show an inhibitory effect on the NOA formation, while others such as chlorogenic acid and gallic acid effectively promote NOA formation[8,9]. Recent work however has demonstrated the possibly universal efficacy of ascorbid acid (**I**) in blocking the formation of nitroso compounds[10]. The mechanism is believed to involve the simple competitive scavenging of nitrosating agent (X=OH, H_2O^+ or NO_2 dependant on pH-value[11]) by **I** (reaction 2). Although reaction 2, originally described by Karrer[12], has more recently been the subject of some very detailed kinetic measurements differing mechanistic interpretations are possible[13].



I II

In view of its obvious importance to a better understanding of the NOA blockage mechanism we are undertaking ESR flow studies of reaction 2. Preliminary results of this work are presented here.



III

Experimental. Ascorbic acid, sodium nitrite and perchloric acid were all of the best commercially available purity and were used without further purification. Extreme