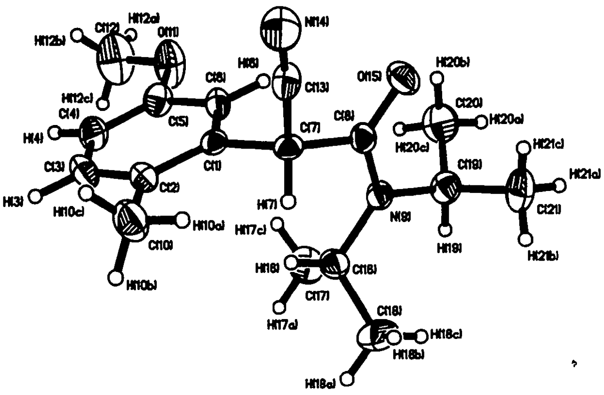

Fig. 1. *ORTEP* (Johnson, 1965) drawing of the molecule. Thermal ellipsoids scaled to enclose 35% probability. H atoms are represented as spheres of arbitrary radii.

Related literature. The mechanism by which compound (1) is formed involves the addition of the anion of α-cyano-*N*,*N*-diisopropylacetamide (formed *in situ* by the reaction of LDA and ethyl cyanoacetate between 195 and 233 K) to 3-methoxy-6-methylbenzyne. To our knowledge, both the addition of an amide to aryne and the low-temperature amination of an ester is unprecedented in the literature. We currently are investigating the mechanism and scope of these novel reactions.

This work was supported, in part, by the Robert A. Welch Foundation under grant N-118 to ERB.

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Structure of Medicagenic Acid: a Triterpene

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Abstract. 2*β*,3*β*-Dihydroxyolean-12-ene-23,28-dioic acid, $C_{30}H_{46}O_6$, $M_r = 502$, orthorhombic, $P2_12_12_1$, $a = 11{\cdot}847\,(1)$, $b = 14{\cdot}654\,(1)$, $c = 15{\cdot}841\,(1)$ Å, $V = 2750{\cdot}1$ Å^3, $Z = 4$, $D_x = 1{\cdot}212\ \text{g cm}^{-3}$, $\lambda(\text{Mo}\ K\alpha) = 0{\cdot}71073$ Å, $\mu = 0{\cdot}47\ \text{cm}^{-1}$, $F(000) = 1096$, $T = 293\,(2)$ K, $R = 0{\cdot}061$ for 1455 independent reflections with $F_o > 2\sigma(F_o)$. The molecule consists of five six-membered fused rings, rings *D* and *E* are *cis*-fused. Ring *C* has a slightly distorted sofa conformation while rings *A*, *B*, *D* and *E* have chair conformations. The H atom at the C(18) asymmetric center is equatorial relative to the *D* ring. The molecules related by the twofold screw axes in the **a** direction are linked 'head-to-tail' *via* intermolecular hydrogen bonds involving the carboxylic groups.

Experimental. The methanol extract of the roots of *Dolichos kilimandscharicus* Leguminosae yielded the saponin 3-*O*-glucosylmedicagenic acid, which on acid hydrolysis gave medicagenic acid. Transparent rectangular crystals were grown from MeOH. Stoe–Siemens AED-2 four-circle diffractometer, $\theta_{\max} = 22{\cdot}5°$. Four check reflections, no intensity variation. Crystal size $0{\cdot}38 \times 0{\cdot}30 \times 0{\cdot}27$ mm. 2555 unique reflections, 1460 with $F_o > 2\sigma(F_o)$, 1455 used for all calculations, five (probably suffering from extinction) removed. Index range h 0–12, k 0–15, l 0–17. Cell constants from $\pm\omega$ values of 56 reflections in the 2θ range 15–27°. No correction for absorption. Structure solved by direct methods using the program system *SHELX*76 (Sheldrick, 1976) which was also used for all further calculations. The –CH and –CH_2 H atoms

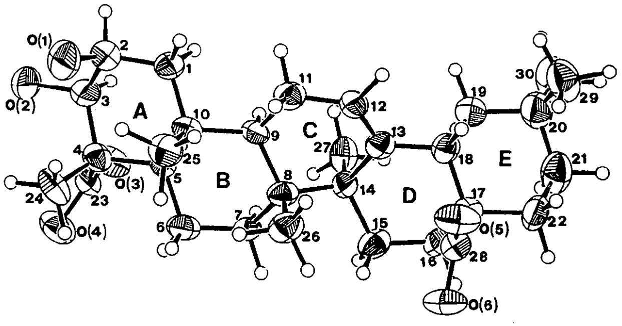

Fig. 1. Perspective view of the molecule, showing atomic numbering scheme (thermal ellipsoids at 50% probability level).

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Table 1. *Final positional and equivalent isotropic thermal parameters* (× 10^4) *of the non*-H *atoms, with e.s.d.'s in parentheses*

$$U_{\rm eq} = \tfrac{1}{3}\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$(Å^2)
O(1)	3213 (4)	5715 (3)	−2080 (3)	764 (21)
O(2)	5107 (5)	5530 (3)	−3034 (3)	809 (21)
O(3)	7051 (4)	4167 (3)	−2242 (3)	755 (21)
O(4)	6074 (5)	3167 (4)	−2974 (3)	779 (21)
O(5)	2962 (4)	2645 (3)	3287 (3)	686 (20)
O(6)	3912 (4)	1413 (3)	2935 (3)	725 (20)
C(1)	4269 (5)	5506 (4)	−737 (4)	465 (23)
C(2)	4282 (6)	5784 (5)	−1663 (4)	561 (28)
C(3)	5150 (6)	5271 (4)	−2171 (4)	517 (25)
C(4)	5029 (6)	4198 (4)	−2079 (4)	481 (25)
C(5)	5076 (6)	3979 (4)	−1113 (4)	412 (22)
C(6)	5134 (6)	2947 (4)	−910 (4)	544 (27)
C(7)	5520 (6)	2821 (4)	−6 (4)	485 (25)
C(8)	4805 (6)	3311 (4)	663 (4)	460 (24)
C(9)	4571 (5)	4311 (4)	378 (4)	400 (23)
C(10)	4191 (5)	4466 (4)	−564 (4)	436 (24)
C(11)	3834 (6)	4799 (4)	1021 (4)	557 (25)
C(12)	4082 (6)	4562 (4)	1915 (4)	472 (25)
C(13)	4762 (6)	3904 (4)	2175 (4)	435 (24)
C(14)	5461 (5)	3353 (4)	1532 (4)	419 (23)
C(15)	5716 (6)	2374 (4)	1856 (4)	567 (27)
C(16)	5946 (6)	2302 (5)	2812 (4)	564 (27)
C(17)	4985 (6)	2727 (4)	3330 (4)	465 (25)
C(18)	4898 (6)	3746 (4)	3122 (4)	497 (25)
C(19)	5869 (6)	4299 (5)	3500 (4)	614 (28)
C(20)	5969 (8)	4211 (6)	4462 (5)	749 (34)
C(21)	6130 (6)	3189 (5)	4648 (5)	785 (34)
C(22)	5208 (6)	2594 (5)	4302 (4)	604 (27)
C(23)	6129 (6)	3839 (5)	−2454 (4)	493 (27)
C(24)	4040 (6)	3789 (5)	−2572 (4)	636 (30)
C(25)	2957 (6)	4140 (5)	−726 (4)	583 (25)
C(26)	3680 (6)	2789 (5)	786 (5)	602 (27)
C(27)	6631 (5)	3844 (5)	1453 (4)	562 (27)
C(28)	3896 (6)	2242 (5)	3177 (4)	518 (27)
C(29)	4975 (8)	4609 (6)	4926 (5)	877 (36)
C(30)	7028 (9)	4709 (8)	4757 (6)	1185 (48)

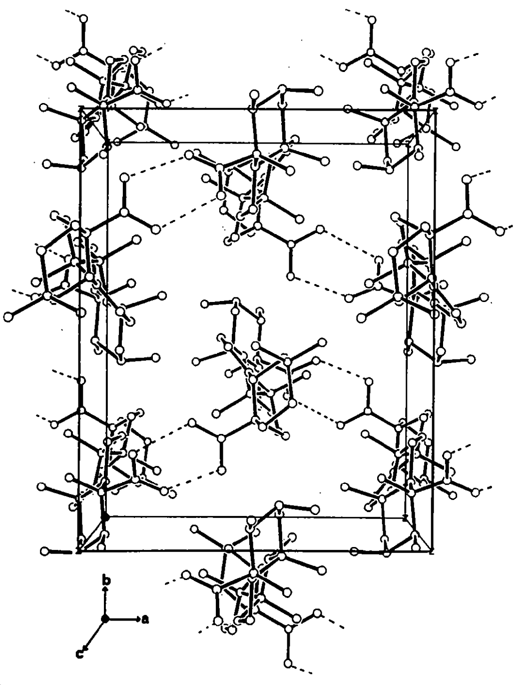


Fig. 2. Packing diagram showing the probable hydrogen-bonding scheme.

Table 2. *Bond distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

C(1)—C(2)	1·522 (9)	C(14)—C(15)	1·553 (8)
C(1)—C(10)	1·552 (8)	C(14)—C(27)	1·568 (8)
C(2)—C(3)	1·507 (8)	C(14)—C(15)	1·553 (8)
C(2)—O(1)	1·431 (7)	C(15)—C(16)	1·543 (9)
C(3)—C(4)	1·586 (9)	C(16)—C(17)	1·535 (9)
C(3)—O(2)	1·419 (7)	C(17)—C(18)	1·533 (8)
C(4)—C(5)	1·564 (8)	C(17)—C(22)	1·574 (9)
C(4)—C(23)	1·526 (10)	C(17)—C(28)	1·493 (9)
C(4)—C(24)	1·530 (9)	C(18)—C(19)	1·530 (9)
C(5)—C(6)	1·548 (8)	C(19)—C(20)	1·533 (9)
C(5)—C(10)	1·538 (8)	C(20)—C(21)	1·538 (10)
C(6)—C(7)	1·514 (9)	C(20)—C(29)	1·507 (11)
C(7)—C(8)	1·536 (8)	C(20)—C(30)	1·524 (10)
C(8)—C(9)	1·557 (8)	C(21)—C(22)	1·503 (9)
C(8)—C(14)	1·582 (8)	C(23)—O(3)	1·240 (8)
C(8)—C(26)	1·549 (8)	C(23)—O(4)	1·287 (7)
C(9)—C(10)	1·576 (8)	C(28)—O(5)	1·267 (8)
C(9)—C(11)	1·520 (8)	C(28)—O(6)	1·274 (7)
C(10)—C(25)	1·560 (9)	O(1)···O(2)	2·719 (7)
C(11)—C(12)	1·487 (8)	O(1)···O(5$^{\rm i}$)	2·837 (6)
C(12)—C(13)	1·323 (9)	O(3)···O(6$^{\rm ii}$)	2·606 (7)
C(13)—C(14)	1·542 (9)	O(4)···O(5$^{\rm ii}$)	2·581 (8)

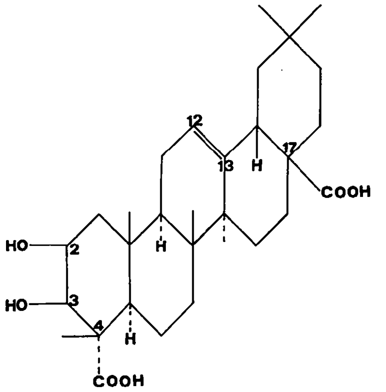
C(10)—C(1)—C(2)	115·6 (5)	C(12)—C(13)—C(14)	120·2 (6)
C(1)—C(2)—C(3)	112·9 (5)	C(12)—C(13)—C(18)	118·8 (6)
C(1)—C(2)—O(1)	114·7 (6)	C(14)—C(13)—C(18)	120·9 (6)
C(3)—C(2)—O(1)	108·8 (5)	C(8)—C(14)—C(13)	109·3 (5)
C(2)—C(3)—C(4)	112·5 (5)	C(8)—C(14)—C(15)	110·3 (5)
C(2)—C(3)—O(2)	110·9 (5)	C(13)—C(14)—C(15)	111·7 (5)
C(4)—C(3)—O(2)	110·5 (5)	C(8)—C(14)—C(27)	112·5 (5)
C(3)—C(4)—C(5)	106·9 (5)	C(13)—C(14)—C(27)	106·7 (5)
C(3)—C(4)—C(23)	103·3 (6)	C(15)—C(14)—C(27)	106·2 (5)
C(5)—C(4)—C(23)	106·2 (5)	C(14)—C(15)—C(16)	114·9 (5)
C(3)—C(4)—C(24)	114·2 (6)	C(15)—C(16)—C(17)	111·5 (5)
C(5)—C(4)—C(24)	116·5 (6)	C(16)—C(17)—C(18)	109·3 (6)
C(23)—C(4)—C(24)	108·7 (5)	C(16)—C(17)—C(22)	110·4 (5)
C(4)—C(5)—C(6)	114·0 (5)	C(18)—C(17)—C(22)	110·0 (5)
C(4)—C(5)—C(10)	115·7 (5)	C(16)—C(17)—C(28)	111·2 (5)
C(6)—C(5)—C(10)	111·4 (5)	C(18)—C(17)—C(28)	111·7 (6)
C(5)—C(6)—C(7)	109·3 (5)	C(22)—C(17)—C(28)	104·1 (5)
C(6)—C(7)—C(8)	115·4 (5)	C(13)—C(18)—C(17)	111·5 (5)
C(7)—C(8)—C(9)	109·8 (5)	C(13)—C(18)—C(19)	112·6 (6)
C(7)—C(8)—C(14)	110·3 (5)	C(17)—C(18)—C(19)	112·4 (6)
C(9)—C(8)—C(14)	107·7 (5)	C(18)—C(19)—C(20)	113·8 (6)
C(7)—C(8)—C(26)	109·3 (5)	C(19)—C(20)—C(21)	106·4 (6)
C(9)—C(8)—C(26)	110·4 (5)	C(19)—C(20)—C(29)	113·1 (7)
C(14)—C(8)—C(26)	109·4 (5)	C(21)—C(20)—C(29)	112·3 (7)
C(8)—C(9)—C(10)	117·4 (5)	C(19)—C(20)—C(30)	109·1 (7)
C(8)—C(9)—C(11)	110·5 (5)	C(21)—C(20)—C(30)	107·8 (8)
C(10)—C(9)—C(11)	113·8 (5)	C(29)—C(20)—C(30)	107·9 (7)
C(1)—C(10)—C(5)	108·4 (5)	C(20)—C(21)—C(22)	113·9 (7)
C(1)—C(10)—C(9)	106·9 (5)	C(17)—C(22)—C(21)	114·0 (6)
C(5)—C(10)—C(9)	105·9 (5)	C(4)—C(23)—O(3)	120·9 (6)
C(1)—C(10)—C(25)	109·1 (5)	C(4)—C(23)—O(4)	118·1 (7)
C(5)—C(10)—C(25)	113·9 (5)	O(3)—C(23)—O(4)	121·0 (7)
C(9)—C(10)—C(25)	112·3 (5)	C(17)—C(28)—O(5)	120·7 (6)
C(9)—C(11)—C(12)	114·5 (6)	C(17)—C(28)—O(6)	119·3 (7)
C(11)—C(12)—C(13)	126·0 (6)	O(5)—C(28)—O(6)	120·0 (7)

Symmetry operations: (i) 0·5$-x$, 1$-y$, $-$0·5 + z; (ii) 0·5 + x, 0·5 $-$ y, $-z$.

were included in idealized positions as riding atoms (C—H 1·08 Å, H—C—H 109·5°) with an overall $U_{\rm iso}$ (refined value 0·0712 Å^2). The methyl groups were included as 'rigid groups' with an overall $U_{\rm iso}$ (refined value 0·1017 Å^2). It was not possible to locate with certainty the —OH or —CO_2H protons. Weighted anisotropic full-matrix least-squares refinement gave $R = 0·061$, $wR = 0·050$, weighting scheme $w = [\sigma^2(F_o) + 0·00072(F_o^2)]^{-1}$. Max. Δ/σ 0·11, mean $<$ 0·04. Max. features in final difference map +0·20, −0·20 e Å^{-3}. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). Atomic coordinates and equivalent isotropic thermal parameters are in Table 1, bond distances and angles in

Table 2.* Figs. 1 and 2, prepared using *ORTEP*II (Johnson, 1976), show a perspective view of the molecule with atomic numbering and the molecular packing, respectively.

Related literature. Medicagenic acid (1) was first isolated from alfalfa (*Medicago sativa*) and was shown to be 2β,3β-dihydroxyolean-12-ene-23,28-dioic acid by various degradations and by a direct correlation with arjunolic acid which has a 2α,3β-orientation (Djerassi, Thomas, Livingston & Thompson, 1957). The molecular geometry of (1) is very similar to that found in the natural compound maytenfolic acid (Nozaki, Suzuki, Lee & McPhail, 1982) and in a synthetic triterpene reported recently (Gzella, Zaprutko, Wrzeciono & Gdaniec, 1986).



(1)

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* Lists of observed and calculated structure factors, anisotropic thermal parameters, H-atom positions and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51422 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Structure of (4*S*)-4-(Methylthio)dibenzothiophene

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Abstract. $C_{13}H_{10}S_2$, $M_r = 230{\cdot}34$, orthorhombic, $P2_12_12_1$, $a = 10{\cdot}732\,(3)$, $b = 14{\cdot}838\,(2)$, $c = 7{\cdot}077\,(1)$ Å, $V = 1126{\cdot}8\,(6)$ Å^3, $Z = 4$, $D_x = 1{\cdot}36$ g cm^{-3}, $\lambda(\mathrm{Mo}\,K\alpha) = 0{\cdot}71069$ Å, $\mu = 4{\cdot}21$ cm^{-1}, $F(000) = 480$, $T = 296$ K, $R = 0{\cdot}037$, 688 unique observed reflections. The compound was prepared by treating 4-lithiodibenzothiophene with dimethyl disulfide. The molecule is a planar dibenzothiophene having a methyl sulfide substituent at the IUPAC C4 position.

Experimental. Preparation by addition of *n*-butyllithium (one equivalent) to dibenzothiophene in THF, solution stirred for 5 h at 273 K. Dimethyl disulfide (one equivalent) added slowly, reaction mixture refluxed for 1·5 h, then stirred at 298 K for 12 h, quenched with water, neutralized with 10% HCl and extracted with dichloromethane. Extract concentrated to give colorless crystals in 70% yield. Crystals suitable for X-ray diffraction grown from dichloromethane with diffusion of a hexane layer. Crystal used for data collection 0·22 × 0·20 × 0·13 mm, clear fragment cut from larger

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