# Determination of Structure and Stereochemistry of Tomentosic Acid by X-Ray Crystallography. A Novel Mechanism for Transformation of Arjungenin to Tomentosic Acid

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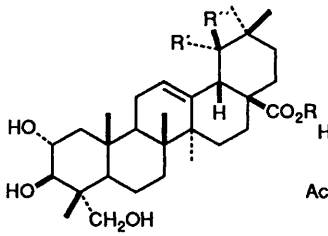
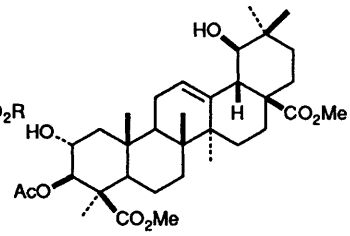
The molecular geometry of tomentosic acid (**1**), a tetrahydroxy triterpene acid obtained by acid hydrolysis of arjunglucoside-I, isolated from *Terminalia bellerica*, has been determined by single-crystal X-ray analysis. The triterpene, $C_{30}H_{48}O_6$, is orthorhombic with space group $P2_12_12_1$ and lattice constants $a$ = 15.994(2), $b$ = 14.682(3), $c$ = 11.494(2) Å, cell volume $V$ = 2 699.0 Å$^3$, and $Z$ = 4. Diffractometer intensity measurements were made with Ni-filtered Cu-$K_\alpha$ radiation, and least-squares adjustment of the atomic parameters converged to a final $R$-value of 0.036. $^{13}$C NMR data are satisfactorily interpreted within terms of the structure. The mechanism of the transformation of arjungenin to tomentosic acid *via* formation of the 28→19 lactone is elucidated. The epimerisation of the 16β-OH group of cochalic acid to its 16α-isomer is also briefly described.



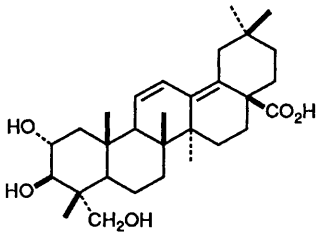
Arjunglucoside-I was isolated as a major product from *Terminalia bellerica* Roxb,[1] reputed for its various medicinal properties.[2] Although arjunglucoside-I (**2**) on alkaline hydrolysis yielded arjungenin (**3**), the normal hydrolysed product, acid hydrolysis of the glucoside generated a major aglycone along with minor products. The m.p. and $[\alpha]_D$-value of the major aglycone compared well with those of tomentosic acid (**1**). However, its formation from arjungenin (**3**) could not easily be understood. Moreover, the $^{13}$C-values of ring-D and -E carbons differed noticeably from those reported for similar carbons of dimethyl 3β-acetoxy-2α,19β-dihydroxyolean-12-ene-24,28-dioate (**4**).[3] These observations reflected some doubt regarding the structure of tomentosic acid. This paper reports the confirmation of the structure and stereochemistry of tomentosic acid by single-crystal X-ray crystallography and elucidation of the mechanism of its formation from arjungenin (**3**).



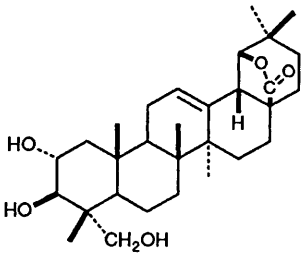

(**1**) R = R' = H, R'' = OH
(**2**) R = β-D-glucose, R' = OH, R'' = H
(**3**) R = R'' = H, R' = OH




(**4**)




(**5**)




(**6**)

## Results and Discussion

Arjunglucoside-I (**2**) on hydrolysis with 5% methanolic hydrochloric acid afforded a mixture of aglycones, which on chromatography over silica gel yielded compound (**1**) and a mixture of aglycones. Two products were separated from this mixture by HPLC. The most probable structure of one of these products is suggested to be 2α,3β,23-trihydroxyoleana-11,13(18)-dien-28-oic acid (**5**) on the basis of its analytical and spectroscopic data. Although an authentic sample of the acid (**5**) was not available for direct comparison its reported spectroscopic data[4] were fairly consistent with those of the isolated sample. The spectroscopic data of the second compound, $C_{30}H_{46}O_5$, strongly suggested its structure to be 2α,3β,19β,23-tetrahydroxyolean-12-ene-28-oic acid 28→19-lactone (**6**). Compound (**1**), m.p. 332 °C; $[\alpha]_D$ +64° (*c* 0.34 in pyridine), appeared to be identical with tomentosic acid.[5] However, as $^{13}$C NMR data of tomentosic acid were not available, assignment of $^{13}$C-values to compound (**1**) was attempted by comparison of the available $^{13}$C data of triterpenes with similar carbon skeletons. The $^{13}$C-values of the ring-A and -B carbons could easily be assigned by comparison with those of arjungenin (**3**).[1] However, there were marked differences in the values of some of the ring-C, -D, and -E carbons between compound (**1**) and dimethyl 3β-acetoxy-2α,19β-dihydroxyolean-12-ene-24,28-dioate (**4**), the only triterpene acid containing a 19β-OH group whose $^{13}$C NMR data have been assigned.[3] The reported data for C-13, C-18, C-19, and C-29 of compound (**4**) are $\delta_C$ 136.0, 45.1, 77.7, and 29.3 respectively, whereas the $^{13}$C data for the corresponding carbons of compound (**1**) assigned by application of known chemical-shift rules,[6] off-resonance decoupling, and intensive nuclei enhancement by polarisation transfer (INEPT) studies are $\delta_C$ 139.5, 49.5, 75.0, and 30.6 respectively. The foregoing observations prompted us to determine the complete structure and stereochemistry of compound (**1**) by single-crystal X-ray crystallography.

The molecular structure of tomentosic acid is shown in an

ORTEP[7] drawing in Figure 1. The atom-numbering scheme and bond lengths are given in Figure 2. Fractional atomic co-ordinates are given in Table 1, and bond angles and a choice of torsion angles are listed in Tables 2 and 3.

The triterpene moiety consists of the five six-membered rings A–E, with a *trans* arrangement for rings A, B, C, and D and a *cis* fusion between D and E. However, as one of the common atoms between rings C and D is on a double bond the *trans* arrangement between these two rings actually indicates that the 27-Me group is *trans* to C-26. It follows from the Cremer–Pople puckering parameters[8,9] (see Table 4) that rings A, B, D, and E have chair conformations (B and E slightly distorted, D remarkably distorted towards a half-chair form), whereas ring C is in a conformation between an envelope and a half-chair (due to the double bond C-12–C-13). With these conformational properties the triterpene skeleton is very similar to the corresponding fragment of asiaticoside which we had previously investigated.[10] The graphical superimposition (with respect to all ring atoms) of both five-ring systems is shown in Figure 3.[11] The geometrical agreement holds also for the substituents except for the $CH_2OH$ group at C-4, which is arranged *trans–gauche* with respect to the ring atoms C-5 and C-3 in the title compound, due to an intramolecular hydrogen bond, but is close to *gauche–gauche* for asiaticoside.

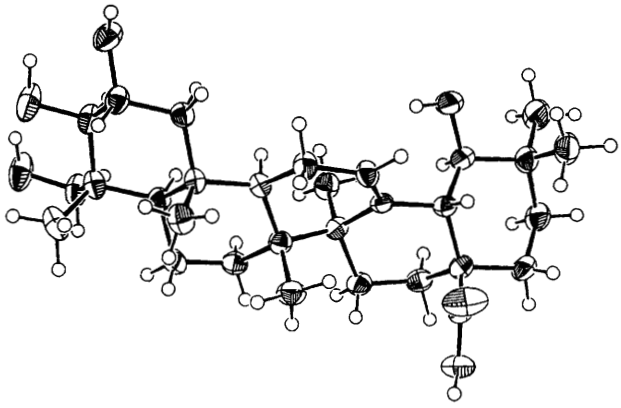


**Figure 1.** ORTEP[7] drawing of the molecular structure of tomentosic acid. The thermal ellipsoids represent a 50% probability level.

The substituents on the triterpene system of the title compound are linked as follows: All OH and $CH_2OH$ groups on rings A and E are in equatorial positions, all methyl groups on rings A–D are substituted axially. The carboxy group at C-17 is axial. The axial methyl groups and the *cis* fusion between rings D and E cause a number of 1,3-diaxial contacts which contribute to some strain in this ring system and which may be responsible for the unusually large C–C bond lengths C-9–C-10 and C-8–C-14, which were also found in asiaticoside.

As Table 5 shows, there exist a number of hydrogen bonds in the crystal structure. The three neighbouring hydroxy groups in ring A are involved in two intramolecular hydrogen bonds, where the hydroxy groups O-23–H-23O and O-3–H-3O act as donors. On the other hand, O-23 is an acceptor and O-2–H-2O is a donor of two intermolecular hydrogen bonds to the carboxy groups of two different symmetry-related molecules. So an accumulation of intra- and inter-molecular interactions is observed on this site of the molecule. Surprisingly, the hydroxy group at C-19 is not involved in the hydrogen-bonding scheme.

After establishment of the structure and stereochemistry of tomentosic acid (**1**), we tried to determine how arjunglucoside-I (**2**) yielded tomentosic acid (**1**) on acid hydrolysis, although on alkaline hydrolysis arjungenin (**3**) was obtained as the only aglycone. Arjungenin (**3**) itself on being boiled with 5% methanolic hydrochloric acid produced tomentosic acid (**1**) as the main aglycone. However, the methyl ester of arjungenin

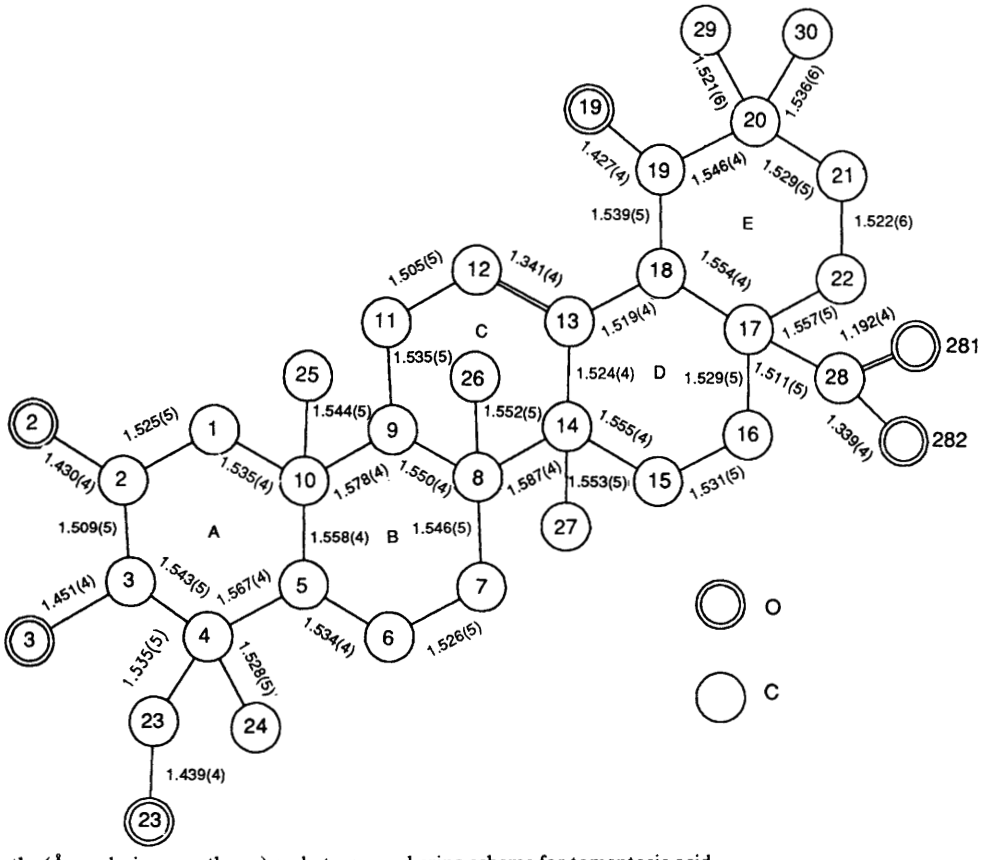



**Figure 2.** Bond lengths (Å, e.s.d.s in parentheses) and atom-numbering scheme for tomentosic acid.

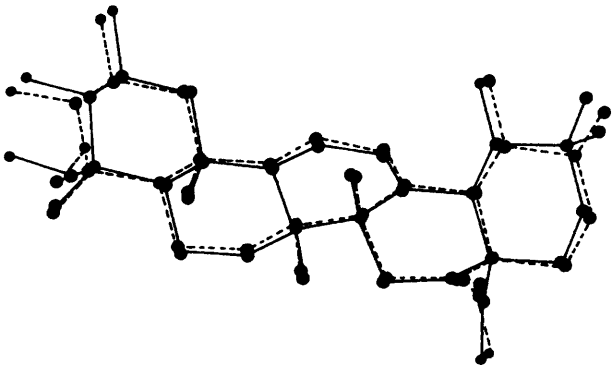


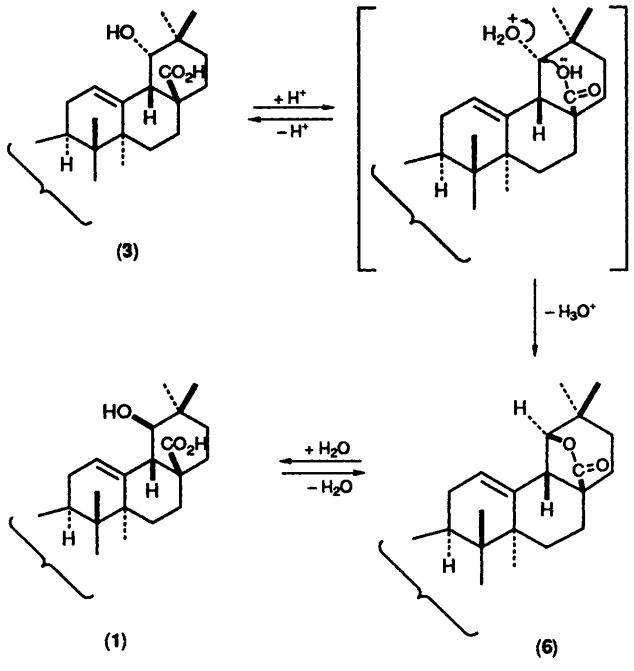
**Figure 3.** Graphical superimposition [11] of the triterpene skeleton for the title compound (——) and asiaticoside (· · · ·).

**Table 1.** Fractional atomic parameters for non-hydrogen atoms.

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| C(1) | 0.188 2(2) | 0.205 1(2) | 0.171 5(3) |
| C(2) | 0.095 5(2) | 0.181 0(2) | 0.172 0(3) |
| O(2) | 0.082 6(2) | 0.086 4(2) | 0.196 1(2) |
| C(3) | 0.051 6(2) | 0.231 4(2) | 0.268 9(3) |
| O(3) | −0.035 7(1) | 0.204 5(2) | 0.270 9(3) |
| C(4) | 0.057 7(2) | 0.336 1(2) | 0.261 6(3) |
| C(23) | 0.026 7(2) | 0.373 5(3) | 0.378 6(4) |
| O(23) | −0.058 0(2) | 0.348 1(2) | 0.405 5(3) |
| C(24) | 0.004 3(3) | 0.375 4(3) | 0.163 5(4) |
| C(5) | 0.153 1(2) | 0.359 4(2) | 0.254 5(3) |
| C(6) | 0.174 3(2) | 0.461 3(2) | 0.251 9(3) |
| C(7) | 0.264 8(2) | 0.475 1(2) | 0.289 9(4) |
| C(8) | 0.330 2(2) | 0.422 3(2) | 0.217 5(3) |
| C(26) | 0.342 3(3) | 0.473 4(3) | 0.100 5(4) |
| C(9) | 0.300 0(2) | 0.323 4(2) | 0.196 0(3) |
| C(10) | 0.205 6(2) | 0.307 6(2) | 0.161 3(3) |
| C(25) | 0.185 2(3) | 0.337 2(3) | 0.035 6(3) |
| C(11) | 0.361 5(2) | 0.273 8(2) | 0.115 4(3) |
| C(12) | 0.451 5(2) | 0.293 7(2) | 0.144 2(3) |
| C(13) | 0.478 3(2) | 0.358 3(2) | 0.218 0(3) |
| C(14) | 0.416 5(2) | 0.417 1(2) | 0.285 4(3) |
| C(27) | 0.407 1(2) | 0.375 6(3) | 0.409 0(3) |
| C(15) | 0.452 3(2) | 0.514 8(2) | 0.301 4(3) |
| C(16) | 0.545 3(2) | 0.517 8(2) | 0.332 9(3) |
| C(17) | 0.598 5(2) | 0.469 9(2) | 0.240 8(3) |
| C(28) | 0.587 6(2) | 0.511 1(2) | 0.121 3(3) |
| O(281) | 0.584 3(2) | 0.469 2(2) | 0.032 6(2) |
| O(282) | 0.586 3(2) | 0.602 3(2) | 0.122 0(2) |
| C(18) | 0.572 0(2) | 0.368 2(2) | 0.235 4(3) |
| C(19) | 0.606 2(2) | 0.314 5(2) | 0.340 1(3) |
| O(19) | 0.583 4(2) | 0.220 8(2) | 0.331 4(3) |
| C(20) | 0.702 4(2) | 0.319 5(2) | 0.351 4(3) |
| C(29) | 0.728 7(3) | 0.268 0(3) | 0.460 2(4) |
| C(30) | 0.746 8(3) | 0.277 6(3) | 0.245 6(4) |
| C(21) | 0.724 0(2) | 0.420 3(3) | 0.366 3(4) |
| C(22) | 0.693 8(2) | 0.479 3(3) | 0.265 8(4) |

**Table 2.** Valence angles (°) (e.s.d.s in parentheses).

| | | | |
|---|---|---|---|
| C(2)–C(1)–C(10) | 113.9(3) | C(11)–C(12)–C(13) | 125.6(3) |
| C(1)–C(2)–O(2) | 111.5(3) | C(12)–C(13)–C(14) | 121.0(3) |
| C(1)–C(2)–C(3) | 110.0(3) | C(12)–C(13)–C(18) | 117.8(3) |
| O(2)–C(2)–C(3) | 105.5(3) | C(14)–C(13)–C(18) | 121.2(3) |
| C(2)–C(3)–O(3) | 109.0(3) | C(8)–C(14)–C(13) | 109.9(2) |
| C(2)–C(3)–C(4) | 114.8(3) | C(8)–C(14)–C(27) | 112.6(3) |
| O(3)–C(3)–C(4) | 109.4(3) | C(8)–C(14)–C(15) | 109.5(2) |
| C(3)–C(4)–C(23) | 106.8(3) | C(13)–C(14)–C(27) | 107.8(3) |
| C(3)–C(4)–C(24) | 112.4(3) | C(13)–C(14)–C(15) | 110.1(3) |
| C(3)–C(4)–C(5) | 106.4(2) | C(27)–C(14)–C(15) | 106.8(3) |
| C(23)–C(4)–C(24) | 109.4(3) | C(14)–C(15)–C(16) | 114.4(3) |
| C(23)–C(4)–C(5) | 106.4(3) | C(15)–C(16)–C(17) | 111.3(3) |
| C(24)–C(4)–C(5) | 115.0(3) | C(16)–C(17)–C(28) | 112.3(3) |
| C(4)–C(23)–O(23) | 113.6(3) | C(16)–C(17)–C(18) | 108.5(3) |
| C(4)–C(5)–C(6) | 115.4(3) | C(16)–C(17)–C(22) | 112.2(3) |
| C(4)–C(5)–C(10) | 117.0(3) | C(28)–C(17)–C(18) | 108.5(3) |
| C(6)–C(5)–C(10) | 110.1(3) | C(28)–C(17)–C(22) | 104.2(3) |
| C(5)–C(6)–C(7) | 109.5(3) | C(18)–C(17)–C(22) | 111.1(3) |
| C(6)–C(7)–C(8) | 114.9(3) | C(17)–C(28)–O(281) | 125.2(3) |
| C(7)–C(8)–C(26) | 108.0(3) | C(17)–C(28)–O(282) | 113.4(3) |
| C(7)–C(8)–C(9) | 110.2(3) | O(281)–C(28)–O(282) | 121.4(3) |
| C(7)–C(8)–C(14) | 110.4(3) | C(13)–C(18)–C(17) | 111.5(2) |
| C(26)–C(8)–C(9) | 110.7(3) | C(13)–C(18)–C(19) | 113.9(3) |
| C(26)–C(8)–C(14) | 109.9(3) | C(17)–C(18)–C(19) | 111.3(3) |
| C(9)–C(8)–C(14) | 107.7(2) | C(18)–C(19)–O(19) | 110.4(3) |
| C(8)–C(9)–C(10) | 118.4(2) | C(18)–C(19)–C(20) | 113.3(3) |
| C(8)–C(9)–C(11) | 109.9(3) | O(19)–C(19)–C(20) | 107.8(3) |
| C(10)–C(9)–C(11) | 113.0(3) | C(19)–C(20)–C(29) | 108.7(3) |
| C(1)–C(10)–C(5) | 109.2(2) | C(19)–C(20)–C(30) | 112.0(3) |
| C(1)–C(10)–C(9) | 107.3(2) | C(19)–C(20)–C(21) | 106.2(3) |
| C(1)–C(10)–C(25) | 107.9(3) | C(29)–C(20)–C(30) | 108.9(3) |
| C(5)–C(10)–C(9) | 105.7(2) | C(29)–C(20)–C(21) | 109.0(3) |
| C(5)–C(10)–C(25) | 113.1(3) | C(30)–C(20)–C(21) | 111.8(3) |
| C(9)–C(10)–C(25) | 113.4(3) | C(20)–C(21)–C(22) | 113.2(3) |
| C(9)–C(11)–C(12) | 112.8(3) | C(17)–C(22)–C(21) | 113.5(3) |




**Scheme 1.** Mechanism for transformation of arjungenin (**3**) to tomentosic acid (**1**).

(**3**) was recovered unchanged after similar acid treatment. Consequently, the epimerisation of 19α-OH was reasonably thought to be *via* lactonisation. Inspection of Dreiding models and isolation of the intermediate lactone (**6**) strongly supported this presumption. The mechanism of transformation of arjungenin (**3**) to tomentosic acid (**1**) is rationalised in Scheme 1. To our knowledge this is the first report of epimerisation of a hydroxy group *via* lactonisation in a triterpene molecule. It may be mentioned that Aoki and Suga [12] reported acid-catalysed epimerisation of the 16β-OH group of cochalic acid. However, they ascribed this phenomenon to thermodynamic stability. It may be mentioned, however, that corchorusin-A, a longispinogenin glycoside,[13] yielded, on acid hydrolysis, the genuine aglycone longispinogenin instead of its 16-epimer, primulagenin A.

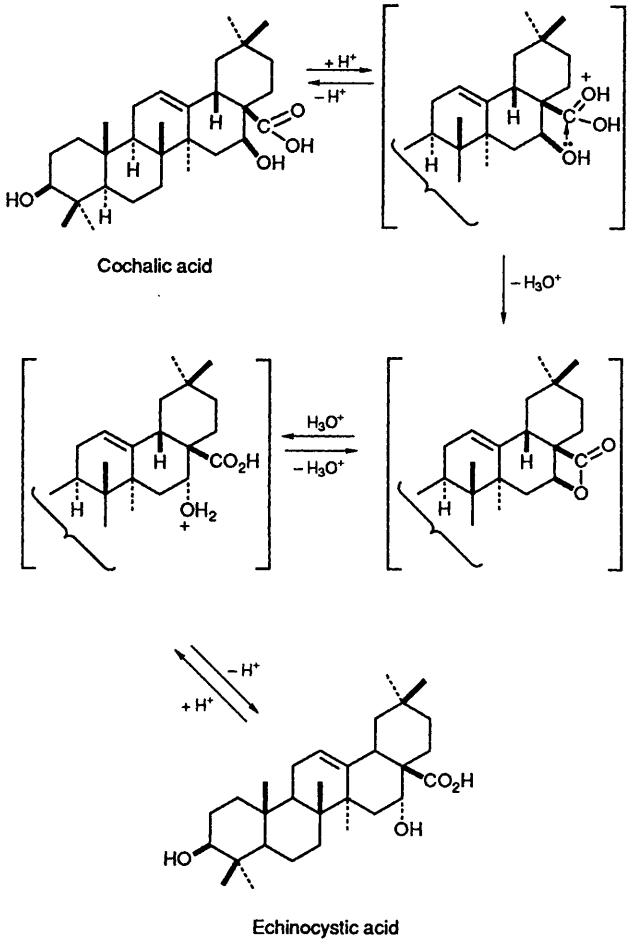
**Table 3.** Dihedral angles (°) (e.s.d.s in parentheses).

| | |
|---|---|
| C(4)–C(3)–C(2)–C(1) | 59.3(4) |
| C(3)–C(2)–C(1)–C(10) | −56.2(4) |
| C(2)–C(1)–C(10)–C(25) | −72.5(3) |
| C(2)–C(1)–C(10)–C(5) | 50.8(3) |
| C(2)–C(1)–C(10)–C(9) | 164.9(4) |
| C(1)–C(10)–C(5)–C(4) | −49.7(6) |
| C(1)–C(10)–C(5)–C(6) | 175.9(3) |
| C(10)–C(5)–C(4)–C(3) | 50.5(4) |
| C(10)–C(5)–C(6)–C(7) | −65.7(4) |
| C(5)–C(4)–C(3)–C(2) | −54.8(3) |
| C(5)–C(4)–C(3)–O(3) | −177.6(2) |
| C(5)–C(4)–C(23)–O(23) | −172.9(3) |
| C(10)–C(5)–C(4)–C(23) | 164.2(4) |
| C(10)–C(5)–C(4)–C(24) | −74.6(4) |
| O(3)–C(3)–C(2)–C(1) | −177.6(4) |
| O(3)–C(3)–C(2)–O(2) | −57.3(3) |
| O(2)–C(2)–C(1)–C(10) | −172.8(3) |
| C(3)–C(4)–C(5)–C(6) | −177.4(3) |
| C(4)–C(5)–C(6)–C(7) | 159.1(3) |
| C(10)–C(5)–C(6)–C(7) | −65.7(4) |
| C(5)–C(6)–C(7)–C(8) | 56.6(4) |
| C(6)–C(7)–C(8)–C(9) | −44.0(4) |
| C(7)–C(8)–C(9)–C(10) | −43.1(3) |
| C(7)–C(8)–C(9)–C(11) | 175.2(4) |
| C(6)–C(7)–C(8)–C(26) | 76.9(4) |
| C(6)–C(7)–C(8)–C(14) | −162.9(3) |
| C(7)–C(8)–C(14)–C(27) | 55.1(3) |
| C(7)–C(8)–C(14)–C(15) | −63.5(4) |
| C(8)–C(9)–C(11)–C(12) | 41.6(4) |
| C(8)–C(9)–C(10)–C(5) | −51.5(3) |
| C(8)–C(14)–C(13)–C(12) | −25.2(3) |
| C(8)–C(14)–C(13)–C(18) | 157.3(2) |
| C(8)–C(14)–C(15)–C(16) | −163.1(3) |
| C(9)–C(10)–C(5)–C(6) | 60.8(4) |
| C(9)–C(11)–C(12)–C(13) | −10.6(7) |
| C(12)–C(13)–C(14)–C(8) | −25.2(3) |
| C(13)–C(14)–C(8)–C(9) | 55.0(5) |
| C(14)–C(8)–C(9)–C(11) | −64.4(6) |
| C(13)–C(14)–C(15)–C(16) | −42.1(4) |
| C(11)–C(12)–C(13)–C(14) | 2.5(5) |
| C(11)–C(12)–C(13)–C(18) | −179.8(6) |
| C(26)–C(8)–C(14)–C(27) | 174.1(2) |
| C(26)–C(8)–C(14)–C(13) | −65.7(2) |
| C(14)–C(15)–C(16)–C(17) | 57.9(4) |
| C(15)–C(16)–C(17)–C(18) | −61.7(3) |
| C(15)–C(16)–C(17)–C(22) | 175.2(3) |
| C(16)–C(17)–C(18)–C(19) | −75.4(3) |
| C(16)–C(17)–C(18)–C(13) | 53.0(3) |
| C(17)–C(18)–C(19)–C(20) | −57.1(3) |
| C(17)–C(18)–C(19)–O(19) | −54.2(5) |
| C(17)–C(18)–C(13)–C(14) | −43.4(4) |
| C(18)–C(13)–C(14)–C(15) | 36.5(4) |
| C(18)–C(19)–C(20)–C(21) | 60.2(4) |
| C(18)–C(19)–C(20)–C(30) | −62.2(4) |
| C(19)–C(20)–C(21)–C(22) | −58.4(4) |
| C(30)–C(20)–C(21)–C(22) | 64.1(4) |
| C(20)–C(21)–C(22)–C(17) | 54.9(4) |
| C(21)–C(22)–C(17)–C(18) | −47.9(4) |
| C(21)–C(22)–C(17)–C(28) | −164.5(3) |
| C(22)–C(17)–C(28)–O(281) | 97.6(4) |
| C(22)–C(17)–C(18)–C(19) | 48.3(3) |
| C(22)–C(17)–C(28)–O(282) | −78.9(3) |
| C(16)–C(17)–C(28)–O(281) | −140.8(4) |
| C(16)–C(17)–C(28)–O(282) | 42.8(4) |

This experiment demonstrated that epimerisation of the 16β-OH group to 16α-OH does not take place on prolonged treatment with acid if there is no 28-$CO_2H$ group available to form the 28→16 lactone. Inspection of Dreiding models also suggested that the 16α-OH (axial) group is not thermodynamically more stable than the 16β-OH (equatorial) group. As such,

**Table 4.** Cremer–Pople puckering parameters of the five six-membered rings of acid (**1**) (e.s.d.s in parentheses). Lower values are for asiaticoside for comparison purposes.

| Ring | $Q$/Å | Θ/° | Φ/° |
|---|---|---|---|
| A | 0.549(4) | 5.1(4) | 332(4) |
| | 0.563(5) | 5.2(5) | 263(5) |
| B | 0.574(4) | 15.6(3) | 7(1) |
| | 0.579(5) | 11.2(5) | 4(3) |
| C | 0.540(3) | 48.9(4) | 45.7(5) |
| | 0.525(6) | 48.8(6) | 50.2(8) |
| D | 0.525(4) | 18.8(4) | 147(1) |
| | 0.534(6) | 18.6(6) | 152(2) |
| E | 0.566(4) | 171.6(6) | 74(3) |
| | 0.550(9) | 174.8(9) | 76(10) |




**Scheme 2.** Proposed mechanism for transformation of cochalic acid to echinocystic acid.

in our opinion, this epimerisation may also occur *via* β-lactonisation between 28-$CO_2H$ and 16β-OH is shown in Scheme 2. Thus in both cases the kinetically controlled products are formed and we suggest that where the lactonisation and delactonisation are possible in a triterpene the kinetically controlled product is obtained exclusively.

## Experimental

M.p.s were determined on a capillary melting-point apparatus and are uncorrected. The $^1H$ NMR spectrum was recorded on a JEOL FX-100 (99.6 MHz) instrument for a $CDCl_3$ solution.

**Table 5.** Hydrogen bonds in tomentosic acid (**1**).

| Sequence | O···O (Å) | O–H (Å) | H···O (Å) | Symmetry operation for second O atom |
|---|---|---|---|---|
| O(23)–H(230)···O(3) | 2.640(4) | 0.94(4) | 1.84(4) | $x, y, z$ |
| O(3)–H(30)···O(2) | 2.706(4) | 1.00(4) | 2.16(4) | $x, y, z$ |
| O(2)–H(20)···O(281) | 2.753(4) | 0.94(5) | 2.00(6) | $\frac{1}{2}+x, \frac{1}{2}-y, -z$ |
| O(282)–H(282)···O(23) | 2.632(4) | 0.92(4) | 1.72(4) | $\frac{1}{2}-x, 1-y, -\frac{1}{2}+z$ |



The $^{13}C$ NMR spectrum was recorded on a JEOL FX-100 Fourier-transform spectrometer operating at 25.05 MHz for a $C_5D_5N$ solution with tetramethylsilane as internal standard. Electron-impact mass spectra were recorded on a JEOL JMS-DX 300 mass spectrometer operating at an ionisation voltage of 30 eV. The IR spectrum was recorded by KBr disc method. Optical rotations were measured on a Perkin-Elmer automatic polarimeter. UV data were for an MeOH solution. HPLC analysis was performed on a Spectra-Physics model 8000 B instrument with a Spherisorb S-10-ODS reversed-phase column (25 cm length, i.d. 10 mm) using a refractive index detector.

*Acid Hydrolysis of Arjunglucoside-I.*—Arjunglucoside-I (**2**) (450 mg), isolated from *T. bellerica* as described previously,[1] was refluxed for 9 h in 5% HCl–aq. MeOH (50 $cm^3$), diluted with ice–water, and extracted with diethyl ether. The extract was worked up as usual to give a mixture of aglycones (255 mg) as evidenced by TLC. This mixture was chromatographed on a silica gel (15 g) column and eluted with 5% MeOH in $CHCl_3$. Thus tomentosic acid (**1**) (100 mg) and a mixture of aglycones were obtained. This mixture was subjected to separation by HPLC with MeCN–water (3:2) as mobile phase (flow rate of 2.2 $cm^3$ $min^{-1}$) to give compound (**5**) (4 mg) and compound (**6**) (6 mg).

*Tomentosic acid* (**1**). This was crystallised from MeOH as prisms, m.p. 332 °C; $[\alpha]_D$ +64° (*c* 0.34 in pyridine) {lit.,[5] m.p. 328–330 °C; $[\alpha]_D$ +64° (*c* 0.32 in EtOH)}; $\delta_C$ 179.2 (C-28), 139.5 (C-13), 126.5 (C-12), 78.3 (C-3), 75.0 (C-19), 68.8 (C-2), 66.7 (C-23), 49.5 (C-18), 48.5 (C-17), 48.0 (C-5), 48.0 (C-9), 47.7 (C-1), 43.5 (C-4), 42.5 (C-14), 39.9 (C-8), 38.3 (C-10), 35.7 (C-20), 35.0 (C-22), 33.0 (C-7), 32.7 (C-21), 30.6 (C-29), 28.2 (C-15), 25.2 (C-11), 24.8 (C-27), 24.0 (C-16), 18.5 (C-6), 17.8 (C-30), 17.5 (C-25), 17.3 (C-26), and 14.2 (C-24) (Found: C, 71.3; H, 9.6. Calc. for $C_{30}H_{48}O_6$: C, 71.39; H, 9.59%).

Methyl ester, m.p. 219 °C; $[\alpha]_D$ +72° (*c* 0.53 in MeOH) {lit.,[5] m.p. 221–222 °C; $[\alpha]_D$ +72° (*c* 0.53)}; *m/z* (rel. int.) 500 ($M^+ - H_2O$) (58%), 482 (5), 441 (15), 405 (8), 278 (11), 260 (29), 246 (29), 219 (21), and 201 (100).

Triacetate, m.p. 179 °C (lit.,[5] 168–186 °C); $\delta_H$ 0.88–1.08 (6 × Me), 1.98 (3 H, s, OAc), 2.01 (3 H, s, OAc), 2.08 (3 H, s, OAc), 5.2 (2β- and 3α-H), and 5.42 (1 H, t-like, 12-H).

2α,3β,23-*Trihydroxyoleana*-11,13(18)-*dien*-28-*oic acid* (**5**). This was obtained as an amorphous solid, $\lambda_{max}$ 243, 253, and 261 (log ε 4.23, 4.16, and 4.27) (Found: C, 74.0; H, 9.6. Calc. for $C_{30}H_{46}O_5$: C, 74.03; H, 9.53%).

2α,3β,19β,23-*Tetrahydroxyolean*-12-*en*-28-*oic acid* 28→19-*lactone* (**6**). This was obtained as an *amorphous solid*, $\nu_{max}$ 3 300–3 500, 1 745 (lactone), 1 160, and 1 060 $cm^{-1}$; *m/z* 486 ($M^+$) (19%), 471 (3), 468 (6), 246 (86), and 201 (100) (Found: C, 74.1; H, 9.5. $C_{30}H_{46}O_5$ requires C, 74.03; H, 9.53%).

*Crystal Data for Tomentosic Acid* (**1**).—$C_{30}H_{48}O_6$, $M_r$ = 504.71, lattice constants (Å) $a$ = 15.994(2), $b$ = 14.682(3), $c$ = 11.494(2), cell volume (Å$^3$) $V$ = 2 699.0, $Z$ = 4, X-ray density (g $cm^{-3}$) $\rho_x$ = 1.242, orthorhombic space group $P2_12_12_1$, total number of reflections 2 504, unobserved [$I < 2\sigma(I)$ 153], linear absorption coefficient μ (Cu-$K_\alpha$) = 6.84 $cm^{-1}$, no absorption correction, $R$-value = 0.036, $R_w$ = $[\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{\frac{1}{2}}$ = 0.031.

*Crystallographic Measurements.*—Suitable single crystals of tomentosic acid (**1**) were obtained from solution in methanol. A prismatic specimen with dimensions 0.15 × 0.15 × 0.35 mm was selected for the X-ray measurements. From preliminary rotation and Weissenberg photographs the space group was determined to be $P2_12_12_1$ crystal system orthorhombic.

Precise lattice constants and the intensity data of an octand ($h, k, l$, all $\geqslant 0$) were measured on a Stoe four-circle diffractometer with Ni-filtered Cu-$K_\alpha$ radiation. Orientation matrix and lattice constants were refined from 42 high-order reflections. The reflection intensities were recorded by the θ–2θ-scan technique with variable scan range and variable scan speed. Three standard reflections, which were measured every 90 min, showed no significant variations during the whole data collection.

*Structure Determination.*—Phase determination was carried out successfully by direct methods (SHELX).[14] All non-hydrogen atoms of tomentosic acid could be identified unambiguously.

Least-squares refinements (with the corresponding programs of the XTAL[15] system) proceeded straightforwardly. First isotropic, and then anisotropic thermal parameters, were assigned to all carbon and oxygen atoms. The hydrogens, which could all be located from difference syntheses, were included with isotropic temperature factors. A $1/\sigma^2(F_o)$ weighting scheme was used with $\sigma(F_o)$ from counting statistics. Unobserved reflections were included in the refinement only if $|F_c| > |F_o|$. After convergence of all parameters a final $R$-value of 3.6% was obtained. The maximum and average shift/error ratios at the end of the refinement were 0.49 and 0.12. A final electron-density map showed all residual density below 0.2 e Å$^{-3}$. The final atomic parameters are given in Table 1. A complete atomic parameter list with anisotropic thermal parameters included and the $F_o$–$F_c$ Tables are deposited at the Cambridge Crystallographic Data Centre.*

* For details see Instruction for Authors, section 5.6.3, in the January issue.

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