Tetrahedron Letters No. 27, pp. 12-16, 1960. Pergamon Press Ltd. Printed in Great Britain

A NEW TRITERPENE CARBOXYLIC ACID FROM
TERMINALIA TOMENTOSA WIGHT *ET* ARN.

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(**Received** 7 **June** 1960; **in revised form** 18 November 1960)

RECENT investigations of King *et al.* on *T. arjuna* Bedd.[1] and *T. ivorensis*[2,3] revealed the presence of two new triterpene carboxylic acids, arjunolic and terminolic acids (I and II).

Among the commercial Indian *Terminalia* species,[4] *T. tomentosa* Wight *et* Arn. is a frequent substitute for teak wood. Although it is credited with fungal resistance, it it not resistant towards white ants. The wood is dark brown, heavy and difficult to work with. Solvent extraction with petroleum ether, ether and acetone was carried out and the extracts fractionated. From the petroleum ether extract, β-sitosterol (m.p. 136-137°; $[\alpha]_D^{31^\circ}$ -35°; acetate, m.p. 126-127°) and oleanolic acid (m.p. 306-309°; $[\alpha]_D^{31^\circ}$ +76°; methyl ester, m.p. 200-202°; acetate, m.p. 260-261°) were isolated. The ether extract could be separated into a new triterpene carboxylic acid (m.p. 328-330°) and a small quantity of a neutral triterpenoid which was not examined any more.

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[1] F.E. King, T.J. King and J.M. Ross, *J.Chem.Soc.* 3995 (1954).

[2] F.E. King, T.J. King and J.M. Ross, *J.Chem.Soc.* 1333 (1955).

[3] F.E. King and T.J. King, *J.Chem.Soc.* 4469 (1956).

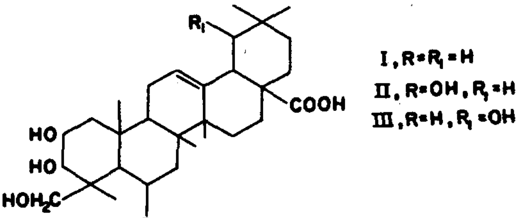
[4] R.S. Pearson and H.P. Brown, *Commercial Timbers of India* Vol. 1, Government of India, Central Publication Branch, Calcutta (1932).

The acetone extract furnished a sparingly soluble colourless solid (yield, 1.5%) identified as arjunolic acid (m.p. 332-334°; $[\alpha]_D^{31^\circ}$ +63°; methyl ester, m.p. 209-211°; $[\alpha]_D^{31^\circ}$ +62°; bromo lactone, m.p. 232-234°; $[\alpha]_D^{31^\circ}$ +53°; bromo lactone triacetate, m.p. 182-183°; $[\alpha]_D^{31^\circ}$ +50°). Our identification of this acid was kindly confirmed by Dr. E. Morgan of British Celanese Ltd. by a mixed melting point and infra-red spectral comparison with an authentic sample of arjunolic acid.

The triterpene carboxylic acid from the ether extract has a molecular formula, $C_{30}H_{48}O_6$. It contained a carboxyl and four hydroxyl groups. It is isomeric with terminolic acid but not identical with it (Table 1) and is therefore named tomentosic acid. The new acid dissolves in conc H_2SO_4 to give a colourless solution initially changing to orange pink in course of time.

Table 1

	Tomentosic acid				Terminolic acid II[2,3]	
	Found	Reqd. for	m.p.	$[\alpha]_D^{31^\circ}$	m.p.	$[\alpha]_D$
Acid		$C_{30}H_{48}O_6$				
	C, 71.8	C, 71.4	328-330°	+ 64°	332-334°	+ 42°
	H, 9.3	H, 9.5				
Methyl ester		$C_{31}H_{50}O_6$				
	C, 71.1	C, 71.8	221-222°	+ 72°	165-168°	+ 40°
	H, 9.9	H, 9.6				
	OMe, 6.3	1-OMe, 6.2				
Epoxide of ester		$C_{31}H_{50}O_7$				
	C, 69.2	C, 69.6	158-160°		175°	+ 7.7°
	H, 9.5	H, 9.3				
Bromolactone		$C_{30}H_{47}O_6Br$				
	C, 61.5	C, 61.7	234-236°	+ 45°	232°	+ 32°
	H, 8.8	H, 8.1				
Anhydrolactone triacetate		$C_{36}H_{52}O_8$				
	C, 70.0	C, 70.6	250-254°	+ 1.8°	211-212°	+ 8°
	H, 8.9	H, 8.6				



Like terminolic acid, tomentosic acid gives a bright yellow colour with tetranitro methane. The infra-red spectrum[5] of the methyl tomentosate revealed characteristic absorption at 11.7 mμ (851 cm^{-1}) and 12.2 mμ (822 cm^{-1}) indicating a trisubstituted double bond.[6]

Tomentosic acid yields both a triacetate and a tetra acetate; but the acetyl derivatives are very difficult to purify and the melting points were never sharp. The methyl ester furnished an isopropylidine derivative (m.p. 168-170°; $[\alpha]_D^{31^\circ}$ +68°; Found: C, 73.5; H, 9.9; $C_{34}H_{54}O_6$ requires C, 73.1; H, 9.7) suggesting a 1:3 diol system in the molecule. Copper pyrolysis at 270-290° gave rise to small quantities of formaldehyde identified as dimedone derivative, thus confirming the presence of 3: 23 **diol** system in the molecule.[7]

Further information regarding the disposition of the hydroxyls in the molecule was secured through periodate and lead tetra acetate oxidations of the methyl ester. From the ease with which periodate was consumed (0.99 mole) and the time (14 hr) required for complete oxidation with lead tetra acetate, it is presumed that the molecule must contain α:β glycol.[8] But the isoproylidine derivative was inert to periodate; the remaining two hydroxyls are, therefore, not in a glycol system. From the foregoing, the presence of

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[5] I.R. spectra reported in this paper were taken in $CHCl_3$ solution on a Cambridge instriument at the National Physical Laboratory, Delhi.

[6] A. Meyer, O. **Jeger** and L. **Ruzicka**, Helv.Chim.Acta 33, 687 (1950).

[7] K. Tsuda and S. Kitagawa, Ber. 71, 1604 (1938).

[8] Carl Djerassi, D.B. Thomas, A.L. Livingston and C. Ray Thompson, J.Amer.Chem.Soc. 79, 5292 (1957).

2α: 3β: 23 (24) -trihydroxy system may be inferred as in arjunolic and terminolic acids.

The following reactions confirm that tomentosic acid belongs to oleanolic acid series of β-amyrin group. (1) The methyl ester is stable to alkali. (2) Tomentosic acid readily furnished a stable bromolactone with bromine in acetic acid.[9] (3) The tetra acetyl methyl tomentosate suffered oxidation with selenium dioxide (1 mole in acetic acid) to give a diene having characteristic triple U.V. absorption maxima (λ_{max} 243, 251, 260 mμ; log ε 4.21, 4.31 4.10).[10] (4) Finally, methyl tomentosate was converted into methyl arjunolate by the following sequence of reactions. 2-Acetyl 3:23 isopropylidine methyl tomentosate was oxidized with pyridine-Cr_2O_3 and the resulting ketone (m.p.204-205°) was reduced by Wolff - Kishner method as modified by Barton *et al.*[11] Removal of the acetyl and isopropylidine groups followed by methylation with diazomethane furnished methyl arjunolate (m.p. 205-207°) undepressed by an authentic sample.

Tomentosic acid undergoes facile lactonization with 50% HBr - acetic acid to give an anhydrolactone diacetate (m.p. 233-235°; $[\alpha]_D^{31^\circ}$ -20°; Found: C, 71.6; H, 8.8; $C_{34}H_{50}O_7$ requires C, 71.6; H, 8.6). Although, the anhydrolactone diacetate or its derivatives did not develop any colouration with tetra nitromethane, it showed a prominent Infra-red absorption for a trisubstituted double bond at 11.6 mμ (861 cm^{-1}) and 12.1 mμ (829 cm^{-1}). Such facile dehydration to produce a trisubstituted double bond may be expected with hydroxyls at 6, 11 and 19 positions only. As tomentosic acid

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[9] O. Jeger, Fortschr.Chem.Org.Naturstoff. **7**, 1 (1950).

[10] D.H.R. Barton and N.J. Holness, J.Chem.Soc. 78, (1952).

[11] D.H.R. Barton, D.A.J. Ives and B.R. Thomas, J.Chem.Soc. 2056 (1955).

is not identical with terminolic acid or its epimer, the 6th position for the fourth hydroxyl is improbable. The 11th position is also excluded since the anhydrolactone triacetate could not be oxidized by pyridine - Cr_2O_3.

Dehydration of triacetyl methyl tomentosate using pyridine - $POCl_3$, benzene - P_2O_5 or selenium dioxide gave rise to a dehydro derivative which was deacetylated and subjected to isomerization with $CHCl_3$ - HCl. The isomeric dehydro tomentosate was not, however, identical with methyl dehydro arjunolate. The methyl dehydrotomentosate (m.p. 198-200°) and its isomer (m.p. 228-230°) gave prominent yellow colouration with tetra nitromethane and possessed a single peak of low intensity at 250 mμ in their U.V. absorption spectra. These reactions seem to exclude the 19th position for the fourth hydroxyl (Fig. III). Tomentosic acid may, therefore, be represented tentatively by 2α : 3β : 23(24): X: tetrahydroxy-olean-12-ene-28-oic acid.

Acknowledgements - Our grateful thanks are due to Prof. F. E. King F.R.S. and to Dr. E. Morgan for confirming our identification of arjunolic acid, to the Director, National Physical Laboratory, Delhi, for the I.R. spectral data and to Prof. T. R. Seshadri F.R.S., Delhi University, Delhi, for U.V. absorption data. We are also grateful to the Council of Scientific and Industrial Research, Delhi, for financial assistance.