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NEW TRITERPENES FROM *BARRINGTONIA ACUTANGULA* GAERTN—III

THE CONSTITUTION OF TANGINOL, A NEW HEXAHYDROXY TRITERPENE

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Abstract—From the wood of *Barringtonia acutangula* Gaertn a new hexahydroxy triterpene, now named tanginol, is isolated besides β- and γ-sistosterols, barringtogenic acid and an unknown triterpene carboxylic acid (compound D).

From a study of several reactions, tanginol is shown to belong to the group of β-amyrins with a 1:2 *cis* glycol at 6β,7β and a 1:3 glycol at 3β,23 positions. The remaining two hydroxyls are also present as a 1:3 glycol and they are located at 16β,28 from analogy Tanginol is, therefore, tentatively shown to be 3β,6β,7β,16β,23,28-hexahydroxy olean-Δ^{12}-ene.

RECENT investigations on *Barringtonia* species[1-6] brought to light several interesting triterpenes of β-amyrin series. It was, therefore, considered of interest to examine the heart-wood of *Barringtonia acutangula* Gaertn. The ether extract of the heart-wood could be separated into β- and γ-sitosterols, a neutral triterpene alcohol (Compound C) and a new trihydroxy triterpene dicarboxylic acid, $C_{30}H_{46}O_7$; m.p. 285°; $[\alpha]_D^{30}$ $+19{\cdot}6°$ (Compound D)*. The former was also isolated from the ethanolic extract, after hydrolysis with 10% aq. H_2SO_4, besides barringtogenic acid[1] and two unidentified triterpenes in minor yield.

Compound C, $C_{30}H_{50}O_6$; m.p. 283–84°; $[\alpha]_D^{30}$ $+9°$, contains six hydroxyls and yields readily a pentabenzoate (III), whose IR spectrum (3555 cm^{-1}) reveals a free hydroxyl group. Acetylation with Py + Ac_2O at 0° yielded a triacetate; but under the catalytic influence of perchloric acid it was possible to secure a hexaacetate (II). Of these six hydroxyls, two are primary as tanginol reacts with tritylchloride to give a ditryl derivative. These facts suggest that it is a new hexahydroxy triterpene, now named Tanginol and the structure (I) is tentatively assigned to it on the basis of the following evidence.

Tanginol (I) contains a trisubstituted double bond (ν_{Nujol} 1660, 844, 808 cm^{-1})[7] resistant to hydrogenation (Pt–H_2) but yielding readily an epoxide with mono-

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* Part IV under communication.

[1] R. Anantha Raman and K. S. Madhavan Pillai, *J. Chem. Soc.* 4369 (1956).

[2] Yau-tang Lin, Tung BinLe and Suchan Su, *J. Chinese. Chem. Soc. Taiwan* Ser. II, **4**, 77 (1957).

[3] T. Nozoe and T. Kinugasa, *J. Chem. Soc. Japan* **56**, 689, 705, 864, 882 (1935).

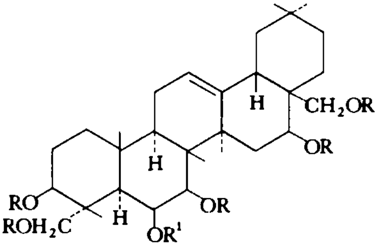
[4] A. K. Barua, S. K. Chakraborti, P. Chakraborti and P. C. Maiti, *J. Ind. Chem. Soc* 483 (1963).

[5] S. K. Chakraborti and A. K. Barua, *Tetrahedron*, **19**, 1727 (1963).

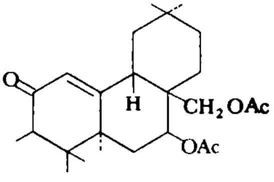
[6] A. K Barua and P. Chakraborti, *Tetrahedron*, **21**, 38 (1965).

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

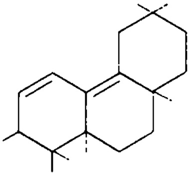
perphthalic acid. During oxidation with CrO_3–HOAc, the hexaacetyl tanginol (II) affords an α,β unsaturated ketone (λ_{max}^{EtoH} 246 mμ, log ε 3·93, ν_{Nujol} 1674 cm^{-1}), which may, therefore, be regarded as hexaacetyl-11 keto-olean-12-ene (IV), thus relegating tanginol (I) to the group of β-amyrins.[8] Furthermore, like β-amyrins[9, 10] hexaacetyl tanginol (II) suffers dehydrogenation when refluxed with SeO_2–HOAc to yield heteroannular $\Delta^{11,13(18)}$ diene (V) with a triple UV maxima at 244, 251 and 260 mμ (log ε, 4·19, 4·32 and 4·08).



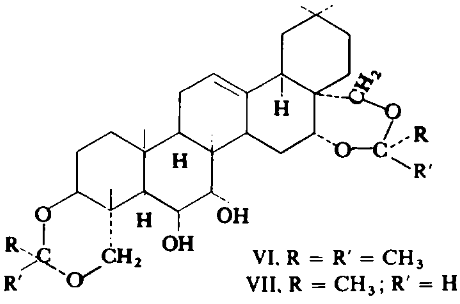
I, R = R′ = H
II, R = R′ = Ac
III, R = Bz, R′ = H
XII, R = H, R′ = Ac



IV



V



VI, R = R′ = CH_3
VII, R = CH_3; R′ = H

Tanginol (I) contains two 1:3 diol systems, since it gives rise to a diisopropylidene derivative (VI) and a diethylidene derivative (VII) and also formaldehyde during copper pyrolysis.[11] The remaining pair is present as a 1:2 *cis* glycol as could be judged by the quick absorption of a mole of periodate (1 hr)[12] or a mole of lead tetraacetate (4 hr)[13] by tanginol (I) and its diisopropylidene derivative (VI). Thus tanginol (I) has two 1:3 and a 1:2 *cis* glycol systems having no common hydroxyl to each other.

The position of 1:2 *cis glycol*

The two hydroxyls of the 1:2 *cis* glycol are not fortunately equivalent in their reactivity. The diisopropylidene derivative (VI) yields only a monobenzoate (VIII)

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[8] L. Ruzicka, G. Müller and H. Schellenberg, *Helv. Chim. Acta* **22**, 758 (1939).

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

[10] A. Sandoval, A. Manjarrez, P. R. Leeming, G. H. Thomas and C. Djerassi, *J. Am. Chem. Soc.* **79**, 4468 (1957).

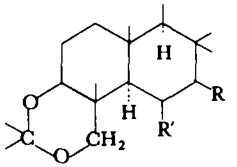
[11] K. Tsuda and S. Kitagawa, *Ber. Dtsch. Chem. Ges.* **71**, 1604 (1938).

[12] C. Djerassi and R. Ehrlich, *J. Org. Chem.* **19**, 1351 (1954).

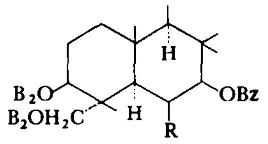
[13] R. Crigee, J. Kraft and Rank, *Liebig's Ann.* **507**, 159 (1933).

and a monoacetate (IX). The former (VIII) is readily oxidized to an unreactive amorphous ketone (X). Likewise, the 0-pentabenzoyl tanginol (III) undergoes facile oxidation with CrO_3–Py to give a ketone (XI) (λ_{max}^{EtOH} 230 mμ log ε (4·79), 275 mμ (log ε 3·72), ν_{CHCl_3} 1742, 1682 cm^{-1}), which is equally unreactive towards any ketonic reagent, suggesting prominantly hindered position for the keto group and hence for the hydroxyl.

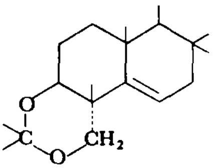
The resistant character of this hydroxyl is also reflected in the behaviour of hexaacetyl tanginol (II) during alkaline hydrolysis, when a monoacetate (XII) is formed within 45 min. The latter does not also react with periodate, suggesting that it could be the same hydroxyl of the 1:2 *cis* glycol which was resistant to acetylation and yielded an unreactive ketone (X) (See above). This is characteristically reminiscent of the behaviour of 6-hydroxyl in sumaresinolic acid (XIII)[14] and terminolic acid (XIV)[15], 6β acetates of which require longer time (24 hr refluxing with 7% alc. alkali) for complete hydrolysis.



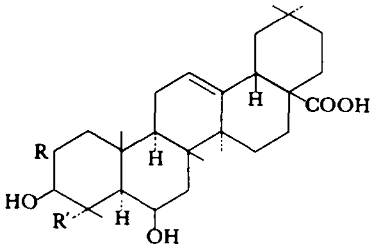
VIII, R = OBz; R' = OH
IX, R = OAc; R' = OH
X, R = OBz; R' = (=O)



XI, R = (=O)



XV, R = OH
XVI, R = (=O)



XIII, R = H; R' = CH_3
XIV, R = OH(α); R' = CH_2OH

These reactions of 1:2 *cis* glycol system in tanginol could be explained satisfactorily, only if it is located at 6,7. The alternate 15,16 or 21,22 positions are straightaway excluded by their well-known easy accessibility towards acetylation.[16, 17]

Further, the monoacetate of 0:0 diisopropylidene tanginol (IX) was refluxed with Py–$POCl_3$ (4 hr) and the resulting product deacetylated to give diisopropylidene anhydro tanginol (XV), which is characteristically inert, to catalytic hydrogenation. It could readily be oxidized with Py–CrO_3 at lab temp to give an α:β unsaturated ketone (XVI λ_{max}^{EtOH} 241 mμ, log ε 4·18).[14, 15] There is no doubt, therefore, that tanginol

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[14] L. Ruzicka, O. Jeger, A. Grob and H. Hosli, *Helv. Chim. Acta* **26**, 2283 (1943).

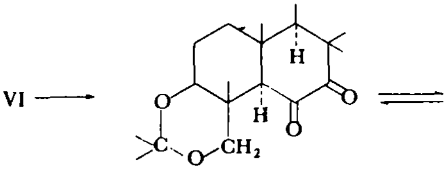
[15] F. E. King and T. J. King, *J. Chem. Soc.* 4469 (1956).

[16] H. M. Smith, J. M. Smith and F. S. Spring, *Tetrahedron* **4**, 111 (1958).

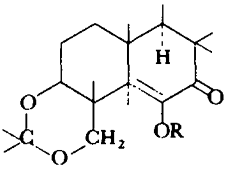
[17] J. O. Knight and D. E. White, *Tetrahedron Letters* No. 3, 100 (1961).

has a 6β-hydroxyl as in sumaresonolic[14] or terminolic acid (XIV)[15] and a 6β,7β *cis* glycol system.

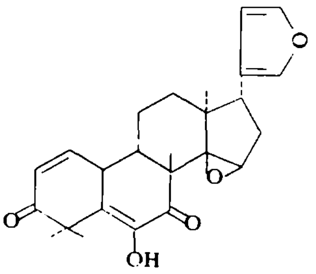
The *cis* glycol system in diisopropylidene tanginol (VI) is also readily oxidizable (Py–CrO_3) to an orange yellow diketone (XVII), IR 1719, 1667 cm^{-1} for diosphenol (Cf. cedrelone, XX)[18] whose reactions suggested a prominent enolic character (XVIII) (brown ferric reaction and a benzoate (XIX); λ_{max}^{EtOH} 230, 271 mμ (log ε 4·1, 3·3). Enolization is possible only if it is a 6:7 diketone, thus finally excluding 15,16 and 21,22 positions for the *cis* glycol system. It is interesting to remark here that similar enolization of 6-keto group was not reported in 3-acetyl-6-keto sumaresinolic lactone (XXI). But Ruzicka[14] showed that when the latter (XXI) was oxidized with SeO_2 in dioxane in a sealed tube at 200°, a diketone (XXII) was obtained which showed enolic reactions ($FeCl_3$: brown).



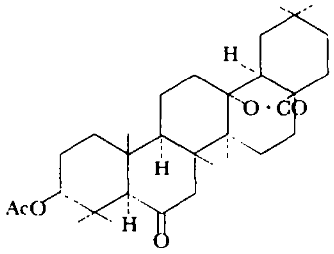
XVII



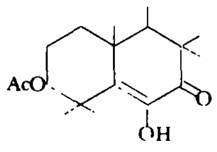
XVIII, R = H
XIX, R = Bz



XX



XXI



XXII

Confirmation of 6β,7β *cis* glycol system in tanginol is readily furnished by its close similarity to terminolic acid (XIV) from *Terminalia ivorensis*.[15] When the ketone (X) from 0:0 diisopropylidene tanginol monobenzoate (VIII) is suspended in methanol and two drops of Conc. HCl added, a colourless crystalline solid (XXV) was obtained which analysed for $C_{37}H_{50}O_6$. The compound showed no C=O absorption in IR spectrum (excepting for 1726 cm^{-1} for benzoyl) and the analysis is consistent with loss of a molecule of water probably through a ring closure. Further on alkaline hydrolysis, an amorphous product (XXVI) was obtained which did not consume any sodium metaperiodate, indicating the absence of *cis* 1:2 glycol system. It is obvious that the ring closure should have taken place between 6-keto group and

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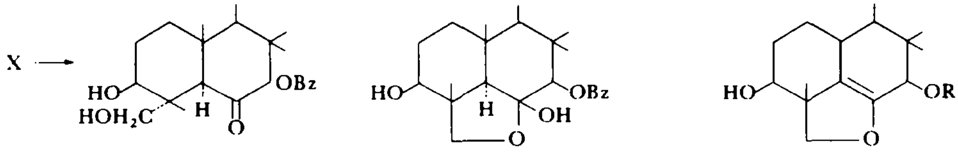
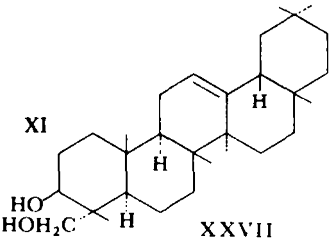
[18] I. G. Grant, J. A. Hamilton, T. A. Hamor, R. Hodges, S. G. McGeachin, R. A. Raphael, J. M. Robertson and G. A. Sim, *Proc. Chem. Soc.* 444 (1961).

23-α-hydroxy methyl group (XXIII) released by HCl hydrolysis of the isopropylidene group. The course of the reaction may be represented by the scheme given below.



XXIII XXIV XXV, R = Bz
XXVI, R = H



XI

XXVII

The ring closure between the 6-keto group and the 23-α-hydroxy-methyl group is reminiscent of the acid induced hemiacetal (XXIV) formation and in this case, it is accompanied by elimination of a mole of water establishing a double bond between 5 and 6 positions.*

The position of 1 :3 *diols*

As an immediate consequence of this ring closure, it may be taken that 3β-hydroxyl and 23-α-hydroxy methyl together constitute one of the two 1 :3 diols in tanginol (I).

The foregoing evidence definitely fixes 3β,6β,7β,23-hydroxyls in tanginol. But the position of the remaining 1 :3 glycol system could be deduced largely from analogies. It could be placed at 16β,28 positions, which surmise is based upon the fact that almost every triterpene of *Barringtonia* species has the oxidation variant of 28-CH_3 group. It follows, therefore, that tanginol might have 16β-hydroxyl (16α-hydroxyl does not permit acetonide formation) or 22-hydroxyl in addition. But the choice falls on 16β-hydroxyl, for under comparatively milder conditions,

* There is greater probability of a concerted mechanism operating in this ring closure such as:

XXV

The protonic attack on the acetonide system takes place simultaneously with the elimination of 5-α-H, thus establishing 5:6 double bond and consequently coplanarity between C-6, C-5 and C-4 which is no doubt responsible for the 23-α-$\overset{+}{C}H_2$ (and not the axial 24-β-$\overset{+}{C}H_2$) suffering ring closure to give XXV.

like Py–Ac_2O at 0°, tanginol yields only a triacetate and not a tetraacetate which is possible if tanginol has a 22-hydroxyl. In tanginol, 6β,7β-hydroxyls as well as 16β-hydroxyls require stronger acetylating conditions.

An effort is now made to reduce the 6,7 diol in tanginol and secure the tetrol (XXVII) to study any specific reactions of the 1:3 diol systems. 6,7-Diketo-0:0-diisopropylidene tanginol (XVII) was found to be unstable and decomposed under Huang–Minlon procedure of Wolff–Kishner reduction. But under these conditions, 6-keto 0-pentabenzoyl tanginol (XI) as well as 6-keto-7-0-benzoyl-0:0-diisopropylidene tanginol (X) gave rise to a neutral triterpene in low yield (10%), which after hydrolysis, analysed for a tetrol. The latter gave no evidence for the presence of 1:2 *cis* glycol. The yield being very low, complete characterization of the tetrol could not be accomplished. However, it could be represented by XXVII. The formation of tetrol (XXVII) may not be entirely unexpected; but no such observation is recorded during Wolff–Kishner reduction. During a preliminary investigation with 2α-0-benzoyl-3-keto-terpenes, it was noticed that the keto group was alone reduced. But 0-benzoyl benzoin or anisoin gives 1:2 diphenyl ethane under these conditions. Further work is in progress.

EXPERIMENTAL

M.Ps are uncorrected. Optical rotations and UV spectra were measured in 95% ethanol. The compounds described were all purified by chromatography on alumina and dried at 100°/0·2 mm for 6 hr before analysis.

Extraction of the wood of Barringtonia acutangula *Gaertn*

The powdered wood (2 kg) was extracted successively with ether and EtOH.

Removal of ether furnished a pale brown solid (12 g). It was dissolved in MeOH aq (1:2, 800 ml), rendered alkaline with 3% MeOH–NaOH and extracted with ether (8 × 200 ml). The ethereal extract was evaporated to give a pale yellow solid (9 g), which was boiled with light petroleum (3 × 200 ml) and filtered. The petroleum soluble fraction was separated by crystillization from MeOH into compound A (m.p. 145–147°, 30 mg) and compound B (m.p. 134–136°, 50 mg).

The petroleum insoluble residue crystallized from MeOH (4 times) to give colourless crystalline compound C (m.p. 279–281°, 6 g).

The alk layer was acidified with dil HCl (congo red) and the ppt, after three crystallizations from acetone, separated out as colourless prisms (Compound D, m.p. 285°, 0·5 g).

Upon concentration, the EtOH extract (4 l) left a dark brown residue which was refluxed for 6 hr with 4% MeOH–H_2SO_4 (300 ml). The solvent was removed in vacuum and H_2O added. The resulting brown solid (35 g) was continuously extracted with ether and the ether extractables were then separated into alkali soluble and neutral fractions.

To purify, the alkali soluble fraction was esterified with diazomethane and the methyl ester in benzene, passed over a column of alumina (40 g) which was successively eluted with benzene (250 ml) and benzene–ether (2:1, 300 ml). Benzene–ether eluate crystallized from benzene–MeOH as silky needles (Compound E, m.p. 253–254°, 150 mg).

From the neutral fraction, compounds C, F and G were separated by chromatography on an alumina column (37 × 5 cm). Table 1 below gives the details of eluants and the compounds isolated.

TABLE 1

S. No.	Eluant	Solid in mg	m.p.	Mol. form	Compounds
1.	Benzene–ether (1:1, 1l)	15	203–206°	$C_{30}H_{50}O_5$	F
2.	Ethyl acetate–methanol (8:1, 0·8l)	80	259–260°	$C_{30}H_{50}O_4$	G
3.	Methanol (1l)	500	281–283°	$C_{30}H_{50}O_6$	C

Compound A: *γ-sitosterol*

Compound A after two crystallizations from MeOH came out as colourless needles, m.p. 147–148°, $[\alpha]_D^{30}$ −45° (c, 0·6%). Lit[19] for γ-sitosterol m.p. 147–148°, $[\alpha]_D^{30}$ −43·3° (c, 0·5%). (Found: C, 83·65; H, 12·4; $C_{29}H_{50}O$ requires: C, 84·04; H, 12·08%.)

Acetate (Ac_2O–Py) crystallized from MeOH as needles, m.p. 139–140°, $[\alpha]_D^{30}$ −46° (c, 0·7%). Lit.[19] for γ-sitosterol acetate, m.p. 142–143°, $[\alpha]_D^{30}$ −47·7° (c, 0·4%). (Found: C, 81·2; H, 11·1. $C_{31}H_{52}O_2$ requires: C, 81·5; H, 11·52%.)

Compound B: *β-sitosterol*

Compound B after two crystallizations from MeOH separated as colourless prismatic needles, m.p. 136–138°, $[\alpha]_D^{30}$ −35° (c, 0·8%). (Found: C, 84·01; H, 12·3. $C_{29}H_{50}O$ requires: C, 84·04; H, 12·08%.)

The acetate (Ac_2O–Py) crystallized as needles from MeOH, m.p. and m.m.p. with β-sitosterol acetate, m.p. 126–127°, $[\alpha]_D^{30}$ −37° (c, 0·8%). (Found: C, 81·3; H, 11·3. $C_{31}H_{52}O_2$ requires: C, 81·5; H, 11·52%.)

Compound C: *tanginol* (I)

Compound C after two crystallizations from MeOH gave colourless microprisms, m.p. 283–284°, $[\alpha]_D^{30}$ +9° (c, 0·4%). (Found: C, 71·34; H, 10·35. $C_{30}H_{50}O_6$ requires: C, 71·14; H, 9·88%.)

O-triacetyl tanginol

Tanginol (150 mg) in acetic anhydride (3 ml) and dry pyridine (5 ml) was allowed to stand for 12 hr at 0° and then diluted with H_2O. The triacetate (100 mg) crystallized from MeOH as needles, m.p. 205–207°, $[\alpha]_D^{30}$ −27° (c, 0·4%). (Found: C, 68·66; H, 8·62. $C_{30}H_{47}O_6(COCH_3)_3$ requires: C, 68·36; H, 8·86%.)

O-hexa acetyl tanginol (II)

Tanginol (150 mg) was suspended in Ac_2O (3 ml) and a drop of perchloric acid added. After the initial reaction (rise of temperature and discoloration), it was diluted to separate the hexaacetate, which came out as amorphous powder from acetone–petroleum, m.p. 151–153°, $[\alpha]_D^{30}$ −63° (c, 0·6%). (Found: C, 66·2; H, 8·26. $C_{30}H_{44}O_6(COCH_3)_6$ requires: C, 66·48; H, 8·18%.)

O-pentabenzoyl tanginol (III)

Tanginol (100 mg) in pyridine (5 ml) and benzoyl chloride (2 ml) was heated on a water-bath for 1 hr. The pentabenzoate crystallized from EtOH as colourless prisms (40 mg), m.p. 306–308°, $[\alpha]_D^{30}$ +43° (c, 0·4%). (Found: C, 76·3; H, 7·07. $C_{65}H_{70}O_{11}$ requires: C, 76·03; H, 6·82%.)

12:13-*epoxy tanginol*

Tanginol (100 mg) in ether–dioxan (3:1, 20 ml) was treated with ethereal monoperphthalic acid (3 ml, 0·57N) and kept at 0° for 17 days. The mixture was then washed with ½N NaOH, and dried over anhyd K_2CO_3. Removal of the solvent furnished a colourless residue which after two crystallizations from MeOH gave 12,13-epoxy tanginol as cubes, m.p. 257–59°, $[\alpha]_D^{30}$ −21° (c, 0·35%). (Found: C, 69·06; H, 9·42. $C_{30}H_{50}O_7$ requires: C, 68·97; H, 9·57%.)

O-ditrityl tanginol

A solution of tanginol (0·50 g) and triphenyl chloromethane (1·5 g) in dioxan–pyridine (1:1, 16 ml) was heated on the steam-bath for 16 hr. The crude product was isolated with ether and chromatographed on alumina (40 g). Elution with benzene afforded triphenyl carbinol (0·35 g), while benzene–MeOH (8:1, 500 ml) eluted the ditrityl derivative. It crystallized from benzene–MeOH as colourless needles (0·25 g), m.p. 236–238°, $[\alpha]_D^{30}$ +12° (c, 0·4%). (Found: C, 82·58; H, 8·1. $C_{68}H_{78}O_6$ requires: C, 82·44; H, 7·88%.) Elution with MeOH yielded the unconverted tanginol (50 mg), m.p. 282–284°.

0:0-*diisopropylidene tanginol* (IV)

Tanginol (100 mg) was suspended in acetone (20 ml) and anhydrous ether (100 ml), treated with four drops of Conc. H_2SO_4 and kept at 0° for 48 hr. It was diluted with ether, washed with K_2CO_3 aq and then with H_2O, and evaporated. The viscous solid was crystallized from acetone–MeOH as prisms (35 mg), m.p. 273–274°, $[\alpha]_D^{30}$ +16° (c, 0·4%). (Found: C, 74·00; H, 9·84. $C_{36}H_{58}O_6$ requires: C, 73·9; H, 9·9%.)

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[19] H. N. Khastgir, S. K. Sengupta and P. Sengupta, *J. Am. Pharm. Ass.* (*Sci. Ed*) **49**, 562 (1960).

Monoacetate (IX) (Ac_2O–Py) crystallized from MeOH as plates, m.p. 131–133°, $[\alpha]_D^{30}$ −14° (c, 0·5%). (Found: C, 66·16; H, 8·95. $C_{38}H_{60}O_7$ requires: C, 65·75; H, 7·95%.)

Monobenzoate (VIII) (Py–Benzoylchloride) crystallized from EtOH as colourless prisms, m.p. 302–304°. (Found: C, 74·93; H, 8·69. $C_{43}H_{62}O_7$ requires: C, 74·8; H, 8·9%.)

0:0-*diethyledene tanginoi* (VII)

Tanginol (0·5 g) was treated with acetaldehyde (15 ml) and Conc. H_2SO_4 (10 drops) and kept at 0° for 2 days. After the usual working up and chromatographic purification, the diethyledene derivative crystallized from acetone aq as colourless needles, m.p. 266–267°, $[\alpha]_D^{30}$ +3° (c, 0·6%). (Found: C, 72·89; H, 9·3. $C_{34}H_{54}O_6$ requires: C, 73·1; H, 9·66%.)

Hydrolysis of 0-*hexaacetyl tanginol*

(*a*) *Tanginol*. The hexaacetyl tanginol (II) in 20 ml MeOH was refluxed with 2N–KOH for 24 hr. After working up in the usual way, and on crystallization from MeOH, tanginol m.p. and m.m.p. 281–283°, was obtained.

(*b*) 0-*Monoacetyl tanginol* (XII). 0-Hexaacetyl tanginol (50 mg) in MeOH (20 ml) was boiled under reflux with 2N–KOH for 45 min. The solvent was removed under vacuum and the residue washed with H_2O. It crystallized from MeOH as colourless needles, m.p. 270–272°, $[\alpha]_D^{30}$ +3° (C, 0·7). (Found: C, 70·16; H, 9·52. $C_{32}H_{52}O_7$ requires: C, 70·06; H, 9·48%).

0-Monoacetyl tanginol (XII) did not react with sodium metaperiodate aq.

(*c*) 0-*triacetyl tanginol*. The 0-hexaacetyl tanginol (50 mg) in MeOH (15 ml) was heated for 40 min with 1·5 ml of a solution of K_2CO_3 (3·0 g) in 1:1 dioxane–water (40 ml); about 12 ml of MeOH being distilled off during that time. The crude product was chromatographed on alumina (5 g) benzene–MeOH (4:1) eluate gave the triacetate, which crystallized from MeOH as needles, m.p. 263–265°, $[\alpha]_D^{30}$ −11° (C, 0·4%). (Found: C, 68·12; H, 9·08. $C_{36}H_{56}O_9$ requires: C, 68·36; H, 8·86%.)

Oxidations with sodium metaperiodate

(*a*) *Tanginol*. An ethanolic solution of tanginol (200 mg) was treated with sodium metaperiodate aq (0·1N, 10 ml), the vol made up to 50 ml with EtOH and the solution kept in dark at room temperature. Aliquot portions (10 ml each) were removed after ½, 1½, 4 and 24 hr. The excess of periodate was estimated using standard sodium arsenite solution. The compound absorbed 0·975, 0·984, 0·984, 0·984 mole of periodate in the respective intervals.

(*b*) 0:0-*diisopropyledene tanginol* (VI). The above estimation was repeated with 0:0-diisopropyledene tanginol. The compound absorbed 0·816, 1·008, 1·008, 1·008 mole of periodate respectively in ½, 1½, 4 and 24 hr.

Oxidations with lead tetraacetate

(*a*) *Tanginol* (I; 100 mg) in Analar AcOH (20 ml) was treated with 15·2 times the molar excess of $Pb(OAc)_4$, and made up to 50 ml. Periodically samples (10 ml) were removed and the excess $Pb(OAc)_4$ estimated iodometrically. The compound reacted with 0·38, 0·78, 0·973 moles of $Pb(OAc)_4$ in 1, 2 and 4 hr intervals.

(*b*) 0:0-*diisopropyledene tanginol* (VI). This derivative (100 mg) under exactly identical conditions, reacted with 0·41, 0·73 and 0·987 mole of $Pb(OAc)_4$ respectively in 1·2 and 4 hr.

Pyrolysis of tanginol (I)

A mixture of tanginol (0·55 g) and finely divided copper (2·8 g) was heated to 270–290° for 1 hr, in a stream of nitrogen. The evolved gases were passed into a saturated aq solution of dimedone. The ppt (35 mg) crystallized from MeOH as colourless needles, m.p. 186–189°, undepressed by an authentic formaldehyde dimedone derivative.

11-*keto* 0-*hexaacetyl tanginol* (IV)

The 0-hexaacetyl tanginol (II; 200 mg) in acetone (40 ml) was treated at 30° with a solution of CrO_3 (2·5 g in 10 ml H_2O + 0·4 ml H_2SO_4). After 10 min, the ketone was collected and crystallized from MeOH as colourless needles, m.p. 181–183°, $[\alpha]_D^{30}$ −17° (c, 0·4%). λ_{max} 246 mμ, log ε 3·93; ν_{Nujol} 1674 cm^{-1}. (Found: C, 65·4; H, 8·1. $C_{42}H_{60}O_{13}$ requires: C, 65·26; H, 7·8%).

SeO_2 oxidation of 0-*hexaacetyl tanginol* (II)

0-Hexaacetyl tanginol (0·75 g) in A.R. AcOH (35 ml) was refluxed with resublimed SeO_2 (0·4 g) for 17 hr. The metallic selenium was filtered off, solvent removed under reduced pressure and the glassy residue separated from acetone–petroleum ether as amorphous solid, m.p. 158–161°, $[\alpha]_D^{30}$ −142° (c, 0·7%). (Found: C, 66·82; H, 8·76. $C_{42}H_{60}O_{12}$ requires: C, 66·67; H, 8·9%.) (λ_{max} 244, 251, 260 mμ log ε 4·19, 4·32, 4·08 respectively).

6-*Keto* 0-*pentabenzoyl tanginol* (*XI*)

0-Pentabenzoyl tanginol (III; 1·0 g) in pyridine (6 ml) was added to pyridine–CrO_3 complex (10 ml, containing 0·5 g CrO_3) at room temperature. After 1 hr, the brown ppt was filtered off and the filtrate diluted with H_2O. After usual purification, the ketone crystallized from MeOH as colourless needles (0·3 g), m.p. 284–285°, $[\alpha]_D^{30}$ −3° (c, 0·4%). (Found: C, 76·07; H, 7·06. $C_{65}H_{68}O_{11}$ requires: C, 76·15; H, 6·64%.) It did not yield any derivative with either 2:4 dinitrophenyl hydrazine or hydroxylamine hydrochloride.

6,7-*Diketo*–0:0-*diisopropyledene tanginol* (XVIII)

0:0-Diisopropyledene tanginol (VI; 1 g) was oxidized with Py–CrO_3 at room temperature yielding 6,7-diketo–0:0-diisopropyledene tanginol (XVIII) as pale yellow needles from MeOH, m.p. 236–238°. (Found: C, 71·99; H, 9·69. $C_{36}H_{54}O_6 \cdot H_2O$ requires: C, 72·0; H, 9·3%.) (ν_{Nujol} 1667 cm^{-1} for diosphenol.) Ferric coloration—brown.

Benzoate (XIX) (Pyridine–benzoylchloride) crystallized from MeOH as pale yellow needles, m.p. 200–203°, $[\alpha]_D^{30}$ −7° (c, 0·4%). (Found: C, 75·54; H, 7·85. $C_{43}H_{58}O_7$ requires: C, 75·21; H, 8·4%), (λ_{max} 230 mμ log ε 4·1 λ_{max} 271 mμ log ε 3·3).

Cyclization of 6-*keto*-7-0-*benzoyl* 0:0-*diisopropyledene tanginol* (X)

7-0-Benzoyl–0:0-diisopropyledene tanginol (VIII; 0·5 g) was similarly oxidized with Py–CrO_3 at room temperature. The crude ketone (X) was suspended in MeOH (25 ml) and treated with a drop of Conc. HCl. The solid rapidly dissolved. After 1 hr at room temperature, the separated solid (XXV) (0·08 g) was crystallized from aq MeOH, m.p. 148–151°, $[\alpha]_D^{30}$ −2° (c, 0·5%). (Found: C, 73·99; H, 8·387; loss on heating 1·43. $C_{37}H_{50}O_6 \cdot \frac{1}{2}H_2O$ requires: C, 73·89; H, 8·674%; $\frac{1}{2}H_2O$, 1·48%).

0:0-*Diisopropyledene anhydro tanginol* (XV)

The monoacetyl diisopropyledene tanginol (IX; 0·5 g) in dry pyridine (10 ml) was treated dropwise with freshly distilled $POCl_3$ (2 ml) and heated under reflux for 4 hr. It was cooled, diluted with H_2O and extracted with ether. On complete removal of the solvent from the ether extract, a pale yellow mass was obtained which could not be crystallized. It was refluxed with 2N MeOH–KOH for 3 hr on a water-bath and the product isolated by dilution with H_2O. When crystallized from MeOH, 0:0-diisopropyledene anhydrox tanginol (XV) was obtained as needles, m.p. 252–253°, $[\alpha]_D^{30}$ −6° (c, 0·8%). (Found: C, 75·61; H, 10·53. $C_{36}H_{56}O_5$ requires: C, 76·06; H, 9·86%).

7-*Keto*-0:0-*diisopropyledene anhydro tanginol* (XVI)

The above compound (XV; 0·2 g) in dry pyridine (10 ml) was added to pyridine (5 ml) containing CrO_3 (0·2 g) at room temperature and kept aside for 2 hr. Working up in the usual way, the keto compound (XVI) was secured as an amorphous solid from acetone–pet ether, m.p. 149–153°. λ_{max} 241 mμ log ε 4·18.

Modified Wolff-Kishner reduction of 6-*keto*-0-*pentabenzoyl tanginol* (XI) *to tetrol* (XXVII)

Sodium (0·2 g) in diethylene glycol (10 ml) was heated to 180° and completely anhydrous hydrazine (4 ml) was added until the mixture refluxed at 180°. 6-Keto-0-pentabenzoyl tanginol (XI) (0·8 g) was added quickly and the solution refluxed for 12 hr. The temperature was then raised to 210° by distilling some amount of hydrazine and the solution refluxed for 24 hr more. The reaction mixture was diluted with H_2O and the ppt crystallized as colourless needles from EtOH aq, m.p. 154–155°, $[\alpha]_D^{30}$ +4° (c, 0·73%). ν_{CHCl_3} 3620 cm^{-1} for OH. (Found: C, 75·34; H, 10·77. $C_{30}H_{50}O_4$ requires: C, 75·94; H, 10·55%).

7-0-*Benzoyl*-0:0-*diisopropyledene tanginol* (VIII *to tetrol* (XXVII)

Compound (VIII; 500 mg) was oxidized with Py–CrO_3 in the usual way. The resulting 6-keto-7-0-benzoyl-0:0-diisopropyledene tanginol (X) was directly reduced adopting Huang Minlon's procedure.

The product was hydrolysed with alcoholic HCl and the tetrol (XXVII) crystallized from MeOH as needles, m.p. 154–155°, $[\alpha]_D^{30}$ +6°. (Found: C, 75·56; H, 10·83. $C_{30}H_{50}O_4$ requires: C, 75·94; H, 10·55%.) The tetrol is found to be identical with the tetrol (XXVII) obtained above.

Compound D

Compound D, after three crystallizations from acetone, came out as colourless prisms (0·6 g), m.p. 285°, $[\alpha]_D$ +19·6° (c, 0·8%). (Found: C, 69·13; H, 9·3. $C_{30}H_{46}O_7$ requires: C, 69·5; H, 8·9%). Conc. H_2SO_4 → yellow → pink → orange red in 30 min. Liebermann–Buchard → pink to orange red. TNM → pale yellow.

Dimethyl ester (diazomethane) crystallized from MeOH, m.p. 180–182°, $[\alpha]_D^{30}$ +26·5° (c, 1·0%). (Found: C, 69·49; H, 9·46; OCH_3, 10·9. $C_{32}H_{52}O_7$ requires: C, 70·00; H, 9·19 and 2-OCH_3, 11·6%.)

Diacetate (Py–Ac_2O) crystallized from acetone–MeOH as flat needles, m.p. 279–281°, $[\alpha]_D^{30}$ +15° (*c*, 0·6%). (Found: C, 67·34; H. 8·51. $C_{30}H_{44}O_7$ $(COCH_3)_2$ requires: C, 67·7; H, 8·36%).

Examination of compound E: dimethyl barringtogenate

Compound E crystallized from MeOH as silky needles, m.p. 253–254°, $[\alpha]_D^{30}$ +61° (c, 0·8%). Lit.[1] m.p. 253–254°, $[\alpha]_D$ +63°. (Found: C, 72·1; H, 9·3. $C_{32}H_{50}O_6$ requires: C, 72·4; H, 9·5%.) Diacetate (Py–Ac_2O) crystallized from MeOH as thick, stout needles, m.p. 238–240°, $[\alpha]_D^{30}$ +34° (c, 0·4%). (Found: C, 70·5; H, 8·3. $C_{32}H_{48}O_6$ requires: C, 70·3; H, 8·85%).

Reduction of compound E with LAH: *barringtogenol*

To a suspension of $LiAlH_4$ (200 mg) in dry ether (150 ml) in an atmosphere of nitrogen, an ethereal solution of compound E (100 mg, 20 ml) was added dropwise. The mixture was stirred for 2 hr, left overnight and then decomposed by addition of ice-cold dil H_2SO_4 and extracted with ether. The dried ether extract on evaporation gave a glassy residue. It crystallized from MeOH as microprisms, m.p. 290–291°, unchanged by authentic barringtogenol isolated from *Terminalia tomentosa*[20], $[\alpha]_D^{30}$ +20° (c, 1·2%). (Found: C, 75·63; H, 10·8. $C_{30}H_{50}O_4$ requires: C, 75·95; H, 10·55%.)

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[20] L. Ramachandra Row and G. S. R. Subba Rao, *Tetrahedron* **18**, 827 (1962).