The non-saponifiable portion of the neutral fraction from the wood extract was chromatographed on silica, and separated into several fractions that were further purified by $AgNO_3$-silica chromatography and by preparative GLC when necessary. As expected, a series of compounds based on the 8,15-isopimaradiene skeleton was found. The following new, natural products were isolated and identified primarily by their NMR spectra[5] ($CDCl_3$): 8,15-isopimaradiene, δ 0·96, 0·96, 0·88 and 0·85 (four methyl singlets); 8,15-isopimaradien-18-al, δ 1·10, 1·03 and 0·98 (three methyl singlets) and 9·33 (CHO), $[\alpha]_D^{25}$ +108° (*c* 1·0, $CHCl_3$), crystals from pentane had an m.p. 31·5–32°; 8,15-isopimaradien-18-ol, δ 1·00, 0·97 and 0·80 (three methyl singlets) and an *AB* quartet (δ_A = 3·18, δ_B = 3·43; *J* 11 Hz); 18-norisopimara-8,15-dien-4-ol,[6] δ 1·16, 0·97 and 0·93 (methyls at C-4, C-13 and C-10, respectively); and 19-norisopimara-8,15-dien-4-ol,[6] δ 1·18, 1·12 and 0·97 (methyls at C-4, C-10 and C-13, respectively). In addition, a number of minor constituents were also found. Dehydroabietal and dehydroabietol were isolated and identified by NMR comparison with the authentic material; geranylgeraniol was identified by NMR, IR and GLC comparison with authentic material. Abietadiene, palustral and *trans*-communol were tentatively identified by NMR.

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[5] The NMR for all compounds showed the same vinyl pattern as methyl 8,15-isopimaradien-18-oate.[4] HALL, S. F. and OEHLSCHLAGER, A. C. (1972) *Tetrahedron* **28,** 3155 report NMR data for 8,15-isopimaradiene and other diterpene hydrocarbons.

[6] Assignments of the C-4 stereochemistry of the norisopimara-8,15-dien-4-ols are based on the relative shielding of the C-10 methyl by the tertiary alcohol. See ROWE, J. W., NAGASAMPAGI, B. A., BURGSTAHLER, A. W. and FITZSIMMONS, J. W. (1971) *Phytochemistry* **10,** 1647 for the nordehydroabietols and ROWE, J. W., RONALD, R. C. and NAGASAMPAGI, B. A. (1972) *Phytochemistry* **11,** 365 for the norpimar-8(14)-enols. CAPUTO, R., MANGONI, L., PREVITERA, L. and IACCARINO, R. (1971) *Tetrahedron Letters* 3731 have reported that large losses of diterpene aldehydes occur during chromatography on silica or alumina and suggest that norditerpene alcohols are formed as artifacts from the aldehydes. However, in our experience in the chromatography of a number of deterpene aldehydes on silica, we have not observed any significant losses. Diterpene Resin Acids. A Compilation of Infrared, Mass, Nuclear Magnetic Resonance, Ultra-violet Spectra and Gas Chromatographic Data (of the Methyl Esters).

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NEUTRAL TRITERPENES FROM THE GALLS OF *PISTACIA TEREBINTHUS*

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Key Word Index—*Pistacia terebinthus*; Anacardiaceae; galls triterpenes; euphanes; oleananes; dammaranes.

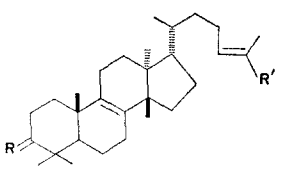
In a previous paper[1] we reported that the acidic fraction of the resin from the galls of *Pistacia terebinthus* is essentially a mixture of known masticadienonic[2] and isomastica-

[1] CAPUTO, R. and MANGONI, L. (1970) *Gazz. Chim. Ital.* **100,** 317.
[2] BARTON, D. H. R. and SEOANE, E. (1956) *J. Chem. Soc.* 4150.

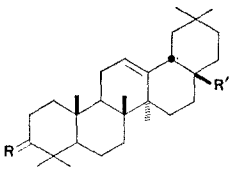
dienonic[3] acids accompanied by smaller amounts of the hitherto unknown isomasticadienolic acid (Ia), its Δ^6 isomer and their respective epimers at C_3.

In pursuing this research, we have now examined the neutral fraction of the resin which at first was roughly separated into three fractions by chromatography: fraction-*A* (25%) eluted with light petrol.; fraction-*B* (55%) eluted with light petrol.–Et_2O (7:3); fraction-*C* (20%) eluted with Et_2O.

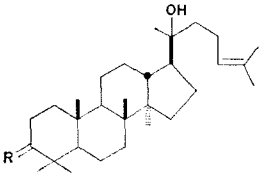
In the present paper we report the results obtained in the investigation of the intermediate polarity fraction-*B*, which appeared to consist of a complex mixture of triterpenic compounds. From this fraction, by chromatography on alumina and, where required, by further separation techniques, nine tetra- and penta-cyclic triterpenes with the euphane, oleanane and dammarane skeletons were isolated.



(Ia) R = H, βOH ; R' = COOH
(Ib) R = H, βOH ; R' = Me
(Ic) R = O ; R' = CH_2OH
(Id) R = H, βOH ; R' = CH_2OH
(Ie) R = O ; R' = COOMe



(IIa) R = O ; R' = CHO
(IIb) R = H, βOH ; R' = CH_2OH
(IIc) R = H, βOH ; R' = CHO
(IId) R = O ; R' = CH_2OH
(IIe) R = O ; R' = COOH
(IIf) R = H, βOH ; R' = COOH



(IIIa) R = O
(IIIb) R = H, βOH

The first substance, a crystalline alcohol with m.p. 132–135°, $[\alpha]_D$ +5° and elemental composition $C_{30}H_{50}O$, was the major component (60%). It was identified as the already known tirucallol (Ib),[4] also by comparison with an authentic sample. The examination of the mother liquors of the crystallization of (Ib) also led to the isolation of another crystalline and extremely unstable substance (8%), with m.p. 138–140°, $[\alpha]_D$ +89° and elemental composition $C_{30}H_{46}O_2$. All the spectroscopic characteristics suggested that it was an unknown ketoaldehyde with the oleanane skeleton, to which it was possible to ascribe the structure (IIa) of oleanonic aldehyde, since its $LiAlH_4$ reduction gave erythrodiol (IIb),[5] m.p. 230–235°.

The chromatography fractions closely following those containing (Ib) and (IIa) gave again a crystalline substance (3%) with m.p. 169–172°, $[\alpha]_D$ +72°, which was identified as the known oleanolic aldehyde (IIc)[5] on the basis of spectroscopic characteristics and through $LiAlH_4$ reduction as well, which led to a quantitative yield of erythrodiol (IIb).

By examining the more polar fractions we were able to obtain a mixture of two substances, no longer separable by chromatography, whose IR spectrum exhibited the ketonic and hydroxyl-adsorptions. The mixture, upon acetylation (acetic anhydride–pyridine) and after chromatography, gave a keto-alcohol (2%) and a keto-acetate (3%). The former was a crystalline solid m.p. 135–136°, $[\alpha]_D$ +67°, identified as dipterocarpol (IIIa)[6] on the basis of the spectroscopic characteristics and through conversion by sodium borohydride into dammarenediol (IIIb)[7] m.p. 142–144°. The oily keto-acetate gave, after hydrolysis, a

[3] SEOANE, E. (1956) *J. Chem. Soc.* 4158.
[4] ARIGONI, D., JEGER, O. and RUZICKA, R. (1955) *Helv. Chim. Acta* 222.
[5] SHAMMA, M. and ROSENSTOCK, P. D. (1959) *J. Org. Chem.* **24**, 726.
[6] CRABBE, P., OURISSON, G. and TAKAHASHI, T. (1958) *Tetrahedron* **3**, 279.
[7] MILLS, J. S. (1956) *J. Chem. Soc.* 2196.

crystalline product with m.p. 189–192°, $[\alpha]_D$ + 85° and elemental composition $C_{30}H_{48}O_2$, to which we ascribed the structure (IId) of 28-hydroxy-β-amirone. Furthermore, the reduction of (IId) by sodium borohydride led to erythrodiol (IIb) while the partial reduction of the oleanonic aldehyde (IIa) (isopropanolic KOH)[8] led to an hydroxyketone which was found to be identical with (IId).

The next substance isolated (3%) was again an oily hydroxy-ketone $[\alpha]_D$ +14°, to which we have ascribed the structure (Ic) of 26-hydroxytirucallone both on the basis of spectroscopic evidences and through $NaBH_4$ reduction which quantitatively gave isomasticadienediol (Id) m.p. 152–154°, $[\alpha]_D$ −7°, already known[9] as a reduction product of methyl isomasticadienonate (Ie).

The last three substances were all diols. Two of them were obtained as a mixture after silica-gel chromatography and it was necessary to isolate them as acetyl derivates. Acetylation gave a monoacetate (4%) and a diacetate (5%) which were easily separated by chromatography. After hydrolysis, they gave dammarenediol (IIIb) m.p. 142–143°, $[\alpha]_D$ +27° and erythrodiol (IIb) m.p. 230–235°, $[\alpha]_D$ +79° respectively, which were compared with authentic samples. The third diol, fairly well separated by chromatography, after crystallization, was a solid (7%) with m.p. 152–154°, $[\alpha]_D$ −7°, which was shown to be isomasticadienediol (Id).

It is noteworthy that in the neutral fraction no traces of Δ^6-euphane compounds were detected. This fact is rather peculiar if we consider that in the acidic fraction the Δ^6- and Δ^7-euphane isomers are present in almost equivalent amounts. Since compounds (IIa–IId) with the oleanane skeleton were found in the neutral fraction, we also checked the possible presence of acids with the same skeleton in the acidic fraction. Actually, the examination of the minor components of the acidic fraction enabled us to isolate small amounts (6% and 2%) of oleanonic acid (IIe)[10] (as its methylester m.p. 181–182°, $[\alpha]_D$ +76°) and oleanolic acid (IIf)[10] (as its methylester m.p. 195–197°, $[\alpha]_D$ +82°), both identified by comparison with authentic samples.

EXPERIMENTAL

M.ps are uncorrected. IR spectra were determined on a Perkin–Elmer mod. 157 spectrophotometer. NMR spectra were recorded on a Perkin–Elmer R 12A spectrometer with TMS as an internal standard. Rotations were taken for $CHCl_3$ (unless otherwise specified) solns at R_t with a Perkin–Elmer mod. 141 polarimeter. TLC were performed on silica-gel F_{254} (Merck). Silica-gel 0·05–0·20 mm (Merck) or alumina (Woelm; grade III unless otherwise specified) was used for column chromatography.

Separation of the neutral components. The neutral extract[1] (27 g), chromatographed on alumina (810 g; grade IV), afforded 3 fractions: a first one (7 g) eluted with light petrol., a second (15 g) eluted with light petrol.–Et_2O (7:3) and a last one (5 g) eluted with Et_2O. The second fraction, rechromatographed on alumina (450 g; 9:1 light petrol.–Et_2O 18 l.) yielded 32 fractions then collected in 6 groups on the basis of TLC and spectral evidences.

Tirucallol (Ib) *and oleanonic aldehyde* (IIa). The crystalline fractions 2–10 (10·3 g), after repeated recrystallizations from MeOH, afforded tirucallol (Ib) m.p. 132–135°, $[\alpha]_D$ +5° (C_6H_6, *c* 1) compared with an authentic sample. The mother liquors of (Ib), after chromatography (silica-gel; hexane–Et_2O, 9:1), gave 1·2 g of crystalline oleanonic aldehyde (IIa) m.p. 138–140° (from MeOH): $[\alpha]_D$ +89° (*c* 1); MW 438 (MS); ν_{max} 1710, 1730 cm^{-1}. (Found: C, 81·98; H, 10·56. $C_{30}H_{46}O_2$ requires: C, 82·13; H, 10·57%); δ 9·35 (1H, *s*, –CHO), 5·30 (1H, *m*, =C=CH–). The $LiAlH_4$ reduction of (IIa) yielded erythrodiol (IIb) m.p. and m.m.p. 230–235°, NMR spectrum identical with that of authentic material.

Oleanolic aldehyde (IIc). Fractions 11–13 (0·5 g), by crystallization from MeOH gave 350 mg of oleanolic aldehyde (IIc) m.p. 169–172°, $[\alpha]_D$ +72° (*c* 1·2). The $LiAlH_4$ reduction of (IIc) gave erythrodiol (IIb) m.p. and m.m.p. 231–235°.

[8] CAPUTO, R. and MONACO, P. (1969) *Rend. Acc. Sci. Mat. Fis. Nat.* **36**, 269.
[9] SEOANE, E. (1956) *J. Chem. Soc.* 4162.
[10] CHEUNG, H. T. and FENG, M. C. (1968) *J. Chem. Soc.* 1047.

Dipterocarpol (IIIa) and *28-hydroxy-β-amyrone* (IId). The oily fractions 14–18 (0·7 g) were a mixture (TLC) of two substances. Their acetylation (acetic anhydride–pyridine at R_t) and chromatography (silica-gel; hexane–Et_2O, 9:1) of the crude product gave a ketoacetate (400 mg) and a ketoalcohol (230 mg). The latter was shown to be dipterocarpol (IIIa) m.p. 135–136°, $[\alpha]_D$ +67° (*c* 1·1) whose reduction by $NaBH_4$ gave dammarenediol (IIIb) m.p. 142–144° compared with an authentic sample. The oily ketoacetate, hydrolysed with methanolic KOH (10%), gave 28-hydroxy-β-amyrone (IId) m.p. 189–192° (from MeOH): $[\alpha]_D$ +85° (*c* 1); MW 440 (MS); ν_{max} 3600, 1710 cm^{-1}. (Found: C, 81·78; H, 10·79. $C_{30}H_{48}O_2$ requires: C, 81·76; H, 10·98%); δ 5·15 (1H, *m*, =C=CH–), 3·35 (2H, *q*, *J* 11 Hz, ≡C–CH_2OH). The $NaBH_4$ reduction of (IId) gave erythrodiol (IIb) m.p. 229–234°. Furthermore, (IId) was prepared by refluxing oleanonic aldehyde (IIa) in isopropanolic KOH (10%) for 2 hr. After additional 8 hr only erythrodiol (IIb) from (IIa) is obtained.

26-Hydroxy-tirucallone (Ic). Fractions 19–21 (0·4 g), after chromatography (alumina; hexane–Et_2O 17:3), gave 300 mg of oily 26-hydroxy-tirucallone (Ic) $[\alpha]_D$ +14° (*c* 1); MW 440 (MS); ν_{max} 1710, 3600 cm^{-1}. (Found: C, 81·82; H, 10·85. $C_{30}H_{48}O_2$ requires: C, 81·76; H, 10·98%); δ 4·08 (2H, *s*, ≡C–CH_2OH). $LiAlH_4$ reduction of (Ic) afforded isomasticadienediol (Id) m.p. and m.m.p. 152–154°.

Dammarenediol (IIIb) *and erythrodiol* (IIb). Fractions 22–26 (1·2 g) were a mixture (TLC) of two substances. After acetylation (acetic anhydride–pyridine at R_t), chromatography (silica-gel; C_6H_6–Et_2O, 4:1) of the crude product gave both oily monoacetate (480 mg) and diacetate (630 mg). The former, after hydrolysis by methanolic KOH (10%), gave dammarenediol (IIIb) m.p. 142–144°, $[\alpha]_D$ +27° (*c* 1·4) compared with authentic material. The diacetate, hydrolysed in the same way, gave erythrodiol (IIb) m.p. 230–235°, $[\alpha]_D$ +79° (*c* 1).

Isomasticadienediol (Id). Fractions 27–32 (0·9 g) gave, after recrystallization from hexane–Et_2O (7:3), isomasticadienediol (Id) m.p. 152–154°, $[\alpha]_D$ −7°; MW 442 (MS); ν_{max} 3600 cm^{-1}. (Found: C, 81·34; H, 11·38. $C_{30}H_{50}O_2$ requires: C, 81·39; H, 11·38%); δ 5·22 (1H, *m*, =C=CH–), 4·08 (2H, *s*, ≡C–CH_2OH) identical with a synthetic sample obtained by $LiAlH_4$ reduction of methyl isomasticadienonate (Ie).

Oleanonic acid (IIe) *and oleanolic acid* (IIf). Acidic extract[1] (10 g) was adsorbed on silica-gel (300 g; HCl washed). Elution with C_6H_6–Et_2O (19:1) gave 580 mg of crude oleanonic acid (IIe) converted by CH_2N_2 into the corresponding methylester m.p. 181–182°, $[\alpha]_D$ +76° (*c* 1) compared with an authentic sample. The subsequent elution with C_6H_6–Et_2O (4:1) then afforded 200 mg of crude oleanolic acid (IIf) which, treated with CH_2N_2, gave the corresponding methylester m.p. 195–197°, $[\alpha]_D$ +82° (*c* 1·3) also compared with an authentic sample.

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QUINONES AND OTHER CONSTITUENTS FROM *TABEBUIA ROSEA*

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Key Word Index—*Tabebuia rosea*; Bignoniaceae; quinones; lapachol; dehydrotectol; dehydro-α-lapachone and isolapachone.

Plant. Tabebuia rosea DC. Voucher specimen No. 11334 deposited in the R.U.B.L. Herbarium. *Previous work.* No work has been reported on this species. On sister species[1,2] *T. flavescens*,[3,4] *T. ipe*,[4] *T. avellanedae*,[5–8] *T. chrysantha* Nichols[9] and *T. doennell* Smittii.[9]

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