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BORON TRIFLUORIDE-CATALYSED REARRANGEMENTS OF SOME TETRASUBSTITUTED NEOTRITERPENE EPOXIDES—I

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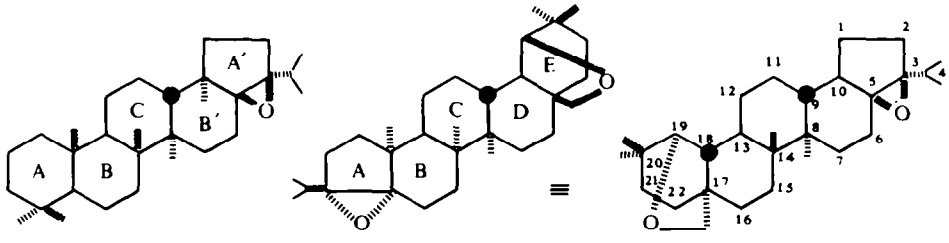
Abstract—The treatment of A'-neogammacer-17(21)-ene oxide (**1a**) with $BF_3 \cdot Et_2O$ complex in $CHCl_3$ produces entirely different results from those obtained when the same epoxide is treated with HCl in EtOH: while the protic acid converts the compound into the 15,17(21)-diene (**2a**), the Lewis acid produces rearrangements in the carbon skeleton, with formation of the 28-nor-21α-methyl-12,17-diene (**3a**) and of the 22,29,30-trisnor-17α-isopropyl-21-one (**4a**). The structurally similar 19β,28-epoxy-A-neo-18α-olean-3(5)-ene oxide (**1b**) behaves in a completely analogous manner.

IN CONNECTION with the structure determination of naturally occurring triterpene epoxides,[1,2] the BF_3-catalysed rearrangements of hopene-I and hopene-II oxides were studied and described in a preliminary report.[3] The results obtained prompted us also to investigate the behaviour of other tetrasubstituted epoxides of the *neo*[4] series toward this reagent. This paper contains the full details of the BF_3-catalysed rearrangements of two such epoxides, having the oxirane ring condensed with the 5-membered ring of the hydrindane moiety, hopene-I oxide (**1a**) and α-apoallobetulin[5] oxide (**1b**). For the latter compound the behaviour towards HCl was also investigated.



1a **1b**

The stereochemistry of rings A', B'[4] and C in compound **1a** is exactly the same as that of rings A, B and C in **1b**.

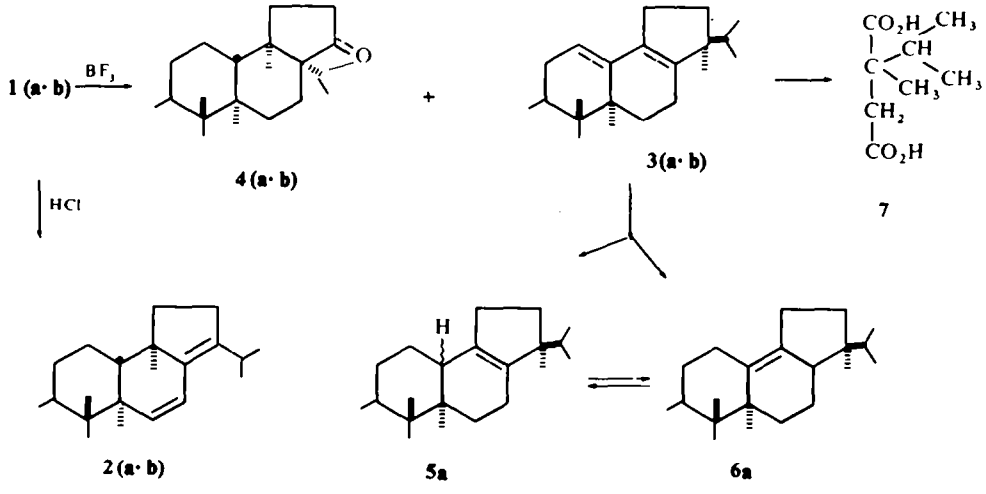
RESULTS

Protic acid treatment of epoxide **1a** leads to the 15,17(21)-diene **2a**.[2] Epoxide **1b** shows an analogous behaviour since it affords, by a similar treatment, the 3(5),6-diene

2b, whose UV (conjugated heteroannular diene) and NMR spectra (AB pattern at δ 5·90 ppm, J_{AB} 10·5 Hz) are very similar to those of **2a**.

Entirely different results are obtained by treating the two epoxides with BF_3-ether complex in chloroform solution. Each compound gives a diene (**3**) and a 5-membered ring ketone (**4**) in the relative amounts of about 85 and 15%. The heteroannular conjugated diene structure of **3a** and **3b** is deduced from their UV spectra; the NMR spectra show only one olefinic proton. Catalytic hydrogenation of **3a** affords an equilibrium mixture of two isomeric olefins (**5a** and **6a**) which can be separated by chromatography over $AgNO_3$-impregnated silica gel. Hydrogen chloride converts each compound into the original equilibrium mixture.

Chart 1



More precise information about the structure of **3a**, **5a** and **6a** derives from their mass spectra.* The most intense peak in the mass spectrum of **3a** (about twelve times more abundant than any other peak) is at *m/e* 365; this originates by the loss of an isopropyl radical from the molecular ion, which is of very low abundance (~ 5%). The formation and the very high abundance of the *m/e* 365 ion (Table 1) provides some indication on the positions of one double bond and of the methyl and isopropyl groups in ring A'. The very easy loss of an isopropyl radical from the molecular ion (in most hopane derivatives the $[M-C_3H_7]^+$ ion is of much lower abundance) could be explained by the fact that this group is linked to a quaternary C atom, and its elimination gives rise to the stable tertiary allylic cation **8** (Chart 2). Almost all other representative fragments in the mass spectrum of **3a** originate from the *m/e* 365 (**8**) ion. Of particular importance for the structure determination of **3a** are two ions of masses 173 and 191, respectively. The former should originate from ion **8** (m* 82) by a retro Diels–Alder cleavage, its structure being very probably **9**. The formation of the latter (**10**), which is usually present in the mass spectra of pentacyclic triterpenes

* The most probable decomposition pathways in these and other mass spectra were supported by the presence of the appropriate metastable ions.

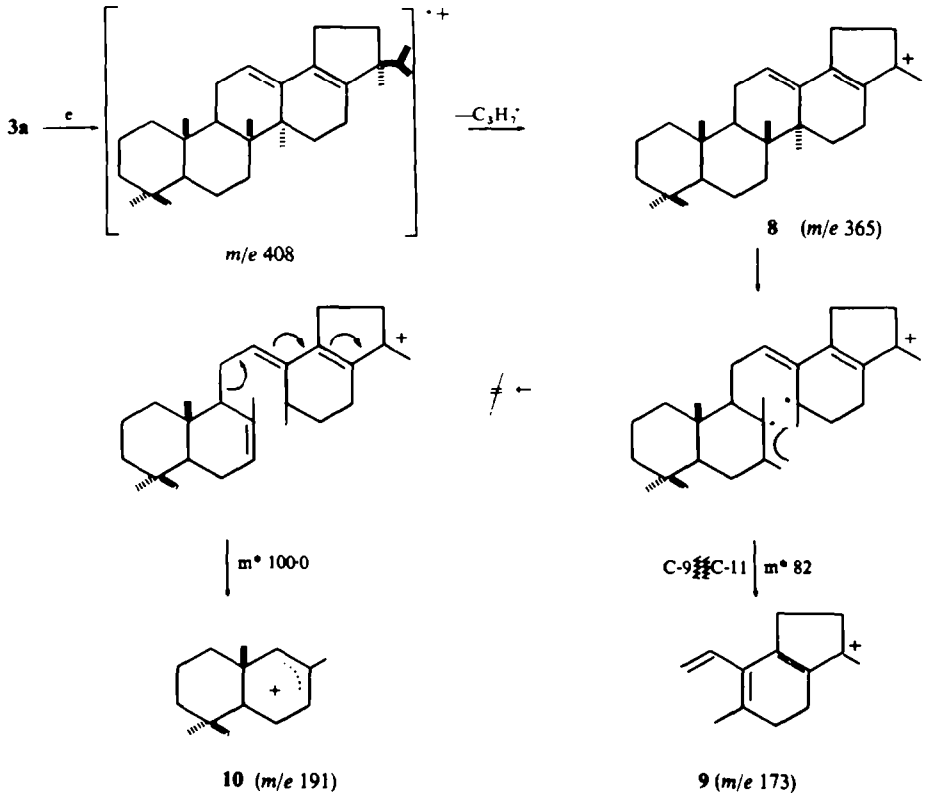
TABLE 1

Compound	$\frac{[M-43]^+}{[M]^+}$	Most abundant ion (*m/e*)
2a	0·11	187
2b	0·11	187
3a	19·0	365 $(M-43)^+$
3b	20·0	379 $(M-43)^+$
5a	35·0	367 $(M-43)^+$
6a	0·45	410 (M^+)
16a	1·18	367 $(M-43)^+$
16b	4·10	381 $(M-43)^+$

having no oxygen in the A and B rings,[6] may be formally represented as indicated in Chart 2.

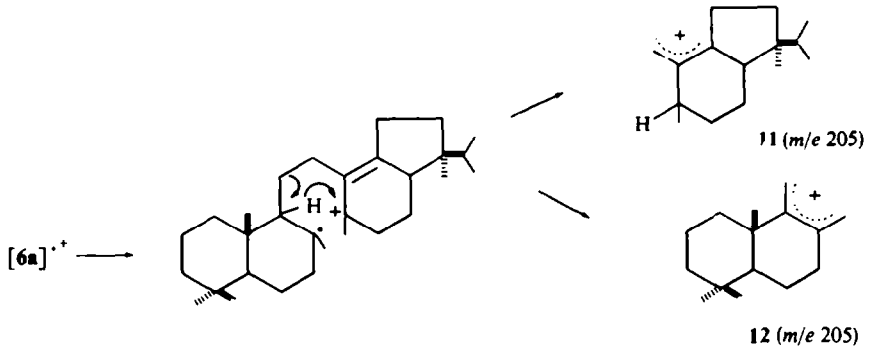
Significant conclusions may also be drawn from the mass spectra of the olefins **5a** and **6a**. The most intense peak in the mass spectrum of the former is at *m/e* 367, corresponding again to the loss of an isopropyl radical from the molecular ion (*m/e*

Chart 2



410), which is of very low abundance (2·9% of the most abundant ion). These features indicate the position of the 17, 18 double bond. In the spectrum of olefin **6a**, in which the double bond is more distant from the isopropyl group, the molecular ion gives the most intense peak whereas the *m/e* 367 ion is of lower abundance (45%). A peak at *m/e* 205 (76% of the most intense peak) is characteristic of triterpenes having a 13,18 double bond, and has been attributed[6] to an ion containing rings D and E (or B′ and A′), formed by allylic cleavage of the 8,14 bond, followed by the cleavage of the 11,12 bond and cyclic collapse with H transfer from C-9 to C-14; this should give ion **11** (Chart 3). However ion **12**, containing rings A and B, is isomeric with **11** and could also contribute to the *m/e* 205 peak. This peak is practically absent from the mass spectrum of **5a**, whereas it is of high intensity in that of hopene-II, whose fragmentation pattern is extremely similar to that of **6a**.

Chart 3



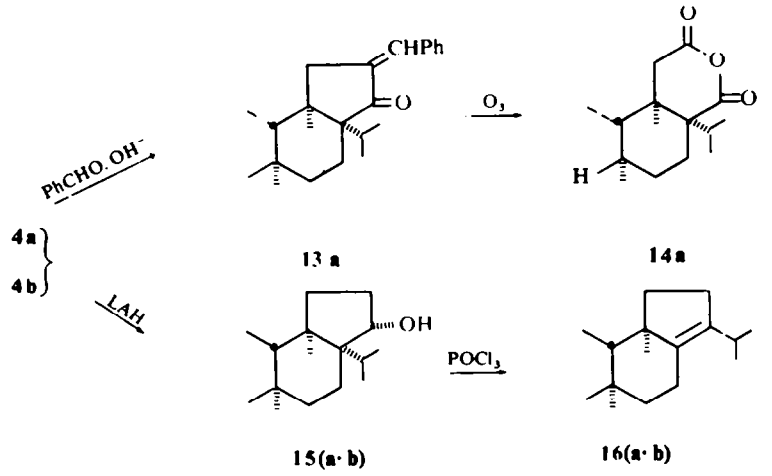
A further proof that a methyl and an isopropyl group are bound to the same C atom (C-21) of **3a** was obtained as follows. Diene **3a** was degraded by oxidation with an excess of CrO_3, followed by ozonolysis. In the acidic fraction of the oxidation product 2-isopropyl-2-methylsuccinic acid (**7**) was detected by TLC, and by GLC of the mixture after esterification with CH_2N_2. Moreover, the mass spectrum of the partially purified methyl esters showed, among other peaks, the same fragmentation pattern as an authentic sample of dimethyl 2-isopropyl-2-methylsuccinate, prepared by the method of Smith and Horwitz.[7]

The mass spectrum of **3b** (Table 1) shows a fragmentation pattern similar to that of **3a**, the most abundant ion being at *m/e* 379, corresponding to the loss of an isopropyl radical from the molecular ion. Also in this case most fragments originate from the *m/e* 379 ion.

The structure of ketone **4a** has been established on the following grounds. It condensed with benzaldehyde in the presence of KOH to give the benzylidene derivative **13a**, which was directly converted by ozone to the anhydride **14a**. Reduction of **4a** with LAH caused transformation into alcohol **15a**. Treatment of the latter with $POCl_3$ in pyridine, instead of producing a simple dehydration, led to the more stable olefin hopene-I (**16a**), with 1,2-shift of the isopropyl group.

An α configuration of the isopropyl group at C-17 in **4a** would be expected from a migration which is concerted with the rupture of the β-oxirane ring. The positive

Chart 4



Cotton effect of moderate intensity of the compound (Experimental) is in accordance with a *cis* junction of rings A′ and B′, on the basis of literature data on compounds containing the *cis*-hydrindane-1-one system, such as 14β-androstan-17-ones and 3-oxo-A-norsteroids,[8] and of recent results obtained in this laboratory.[9] Although the isopropyl group lies in a negative octant, the skewed nature of the cyclopentanone ring should be more important in determining the sign of the Cotton effect than the orientation of the substituents. On the other hand the 17β-isopropyl analogue of **4a** would be expected to exhibit a negative Cotton effect, as was observed in the case of some A-norcholestane derivatives.[9] The conformation of the OH group in **15a** is very probably α, since a determination of absolute configuration with α-phenylbutyric anhydride by Horeau's method[10] gave an excess of (−)-acid, therefore pointing to an (*S*) configuration at C-21. This is somewhat surprising as 17-oxo-14β-steroids are reported to give the 17α-ols on hydride reduction.[10, 11] However, an isopropyl in place of a Me group may well change the stereochemistry of the reduction.

Completely analogous results have been obtained with ketone **4b**: it showed a positive Cotton effect and was reduced to the alcohol **15b**, which gave α-apoallobetulin (**16b**) by action of $POCl_3$.

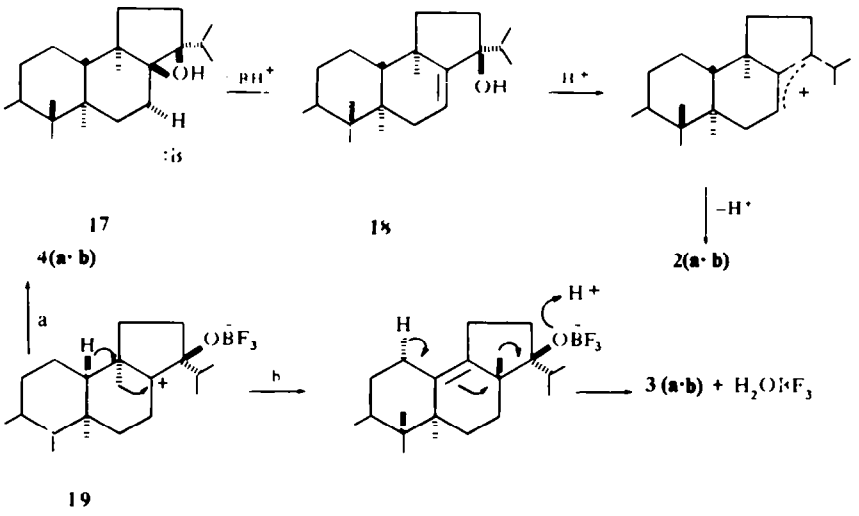
DISCUSSION

One of the interesting points in the rearrangements discussed above is the fact that protic and Lewis acids give completely different products. Although very little can be said on the basis of the data at hand about the sequence of events and the degree of concertedness in the conversion of the epoxides **1a** and **1b** into products, it appears likely that in the more polar medium (EtOH) and in the presence of a protic acid (HCl) a large amount of a proton acceptor facilitates the termination of the reaction without much rearrangement. Thus, the conversions into the dienes **2a** and **2b** could be visualised as involving cleavage of the protonated epoxide (**17**) at C-17, possibly to give the allyl alcohol **18** as an intermediate, dehydration of which would lead to the more stable diene (**2a** or **2b**). Although the epoxides **1a** and **1b** are ditertiary, cleavage at C-17 would presumably be somewhat favoured over cleavage at C-21,

because in the latter case the OH group would be axial with respect to the 6-membered ring.

The behaviour of the two epoxides with BF_3-ether complex is more novel. If one assumes also in this case a cleavage at C-17, in the absence of a good proton acceptor the ion **19** can either give the usual 1,2 shift of the isopropyl group, leading to the ketones **4**, or that of the methyl group at C-18, which would be favoured, because it would relieve the bad non-bonding interaction between the two syn-axial methyl

Chart 5



groups. Intermediate **19** could be converted through a possibly concerted rearrangement-elimination to the dienes **3a** and **3b**. No long-lived intermediates have been detected in any case by GLC, even when the reaction mixtures were quenched after short times. Several other pathways could be depicted, including one involving cleavage of the epoxide at C-21, followed by an unprecedented 1,3 shift of the Me group from C-18 to C-21; but, in the absence of more conclusive evidence, we shall not discuss them.

EXPERIMENTAL

M.ps were determined on a Kofler apparatus. IR spectra were recorded on Nujol mulls with a Perkin–Elmer Infracord, mod 137, spectrophotometer. UV spectra were determined in cyclohexane soln with a Beckman DU spectrophotometer. NMR spectra were registered in $CDCl_3$ (TMS internal standard) with a Varian DA-60-IL spectrometer. Specific rotations were measured in 1% $CHCl_3$ soln at 25° with a Perkin–Elmer, mod 141, photoelectric polarimeter. CD measurements were made in cyclohexane with a Roussel–Jouan dichrograph. GLC analyses of triterpenoidic olefins were performed with a Perkin–Elmer F-20 gas-chromatograph [column: 1% neopentyl glycol succinate (NPGS) on Chromosorb W 80–100 mesh, temp 200°, injection block temp 230°, carrier gas N_2, flow rate 50 ml/min]. Mass spectra were measured with an Atlas CH4 mass spectrometer fitted with TO-4 ion source and direct inlet system, operated without heating. The samples were heated externally, if necessary, until the ion current was sufficient to provide usable mass spectra. The ionization energy was maintained at 70 ev. Pet ether refers to the fraction of boiling range 30–50°.

Hopane series

17,21β-*Epoxy-A'-neogammacerane* (**1a**) was obtained in small yield by chromatography of the pet

ether extract of the fern *Polypodium vulgare* L. over neutral Al_2O_3 (grade II). It was eluted by light petroleum right after the hydrocarbon fractions. Since the yield varied much according to the lot of plant material and of Al_2O_3 and was very low anyway, because of partial conversion into the diene **2a** during chromatography, a better source was found in *adiantone* and *isoadiantone*, easily available from the extract of the fern *Adiantum capillus-Veneris* L.,[12] which were converted respectively into 22-hydroxyhopane and 21αH-22-hydroxyhopane with MeMgI.

A mixture of 22-hydroxyhopane (0·57 g) and PhCOCl (5 ml) was refluxed for 2 hr, then treated with 2N Na_2CO_3 and heated on a steam bath for 30 min. The product was extracted with pet ether, dried ($MgSO_4$), filtered through neutral Al_2O_3 and crystallized from $CHCl_3$—MeOH to give *A'-neogammacer*-17(21)-*ene* (**16a**, 0·42 g), m.p. 176–179°, $[\alpha]_D$ + 47·5°, no olefinic proton in NMR. (Lit.[13] m.p. 178–180°, $[\alpha]_D$ + 49·5°). (Found: C, 88·02; H, 12·11; Calc. for $C_{30}H_{50}$: C, 87·73; H, 12·27%). A similar treatment of 21αH-22-hydroxyhopane (0·23 g) also gave **16a** (0·19 g).

A soln of **16a** (1·2 g, 2·92 mmole) in $CHCl_3$ (60 ml) was treated with 98% *p*-nitroperoxybenzoic acid (0·64 g, 3·4 mmole). After 24 hr at 0° usual work-up gave **1a** (0·9 g, from pet ether), m.p. 268–270°, $[\alpha]_D$ + 48°; IR λ 11·5 μ (epoxide). (Found: C, 84·48; H, 11·90; $C_{30}H_{50}O$ requires: C, 84·44; H, 11·81%).

Rearrangement of **1a** *with* $BF_3 \cdot Et_2O$. A soln of **1a** (0·30 g) in $CHCl_3$ (30 ml) was treated with $BF_3 \cdot Et_2O$ (3 ml), left 4 hr at room temp, then washed with 2N Na_2CO_3, dried ($MgSO_4$) and evaporated. The residue was dissolved in pet ether and chromatographed over neutral Al_2O_3 (grade I). The pet ether eluate gave 28-*nor*-21α-*methyl-A'-neogammacera*-12,17-*diene* (**3a**, 0·24 g), which was crystallized from Me_2CO; m.p. 167–169°, $[\alpha]_D$ + 51°; λ_{max} 237, 245, 255 nm (ε 20,300; 23,700; 15,900); NMR, δ 5·39 ppm (1H). [Found: C, 87·82; H, 12·11; M.W. 408 (MS); $C_{30}H_{48}$ requires: C, 88·16; H, 11·84%; M.W. 408]. Further elution with Et_2O gave 22,29,30-*trisnor*-17α-*isopropyl-A'-neogammaceran*-21-*one* (**3a**, 45 mg) m.p. 278–281° (from $CHCl_3$–MeOH); $[\alpha]_D$ + 86·3°; λ_{CO} 5·79 μ; CD, $\Delta\varepsilon_{323}$ + 0·69, $\Delta\varepsilon_{312}$ + 1·14, $\Delta\varepsilon_{302}$ + 1·06. (Found: C, 84·26; H, 11·81; $C_{30}H_{50}O$ requires: C, 84·44; H, 11·81%).

Yield in **3a** and **4a** did not change appreciably when the reaction time was 25 hr, or when 1/5 of the amount of $BF_3 \cdot Et_2O$ was used and the reaction time was only 5 min.

28-*Nor*-21α-*methyl-A'-neogammacer*-17-*ene* (**5a**) *and* 28-*nor*-21α-*methyl-A'-neogammacer*-13(18)-*ene* (**6a**). A soln of **4a** (0·22 g) in cyclohexane (40 ml) and AcOH (10 ml) was hydrogenated at room temp for 15 hr over 10% Pt-C (0·20 g). Usual work-up gave a mixture of **5a** and **6a** (0·20 g) which was chromatographed over 10% $AgNO_3$–SiO_2, while following the elution with pet ether by GLC. The first fractions gave **6a** (45 mg), m.p. 173–179° (from $CHCl_3$–MeOH), $[\alpha]_D$ − 4·6°, no olefinic H in NMR. [Found: C, 87·45; H, 12·42; M.W. 410 (MS); $C_{30}H_{50}$ requires: C, 87·73; H, 12·27%; M.W. 410]. Further elution yielded mixtures of **5a** and **6a**, then pure **5a**, m.p. 176–179° (from $CHCl_3$–MeOH), $[\alpha]_D$ − 11·7°, no olefinic H in NMR. [Found: C, 87·40; H, 12·49; M.W. 410 (MS); $C_{30}H_{50}$ requires: C, 87·73; H, 12·27%; M.W. 410].

When a soln of either **5a** or **6a** in $CHCl_3$ was saturated with gaseous HCl an equilibrium mixture of 60% **5a** and 40% **6a** was obtained (GLC).

Oxidative degradation of **3a**. To a soln of **3a** (1·0 g) in Me_2CO (150 ml) was added a 8N soln of CrO_3[14] (3·5 ml) with stirring at 40°. After 1 hr the mixture was diluted with H_2O and extracted with Et_2O. The residue obtained by evaporation of the Et_2O was taken up in $CHCl_3$, dried ($MgSO_4$) and evaporated to give an oil (1·2 g), whose IR spectrum had several bands in the 6 μ region; it was dissolved in anhydrous $CHCl_3$ and the soln was subjected to ozonolysis for 4 hr at 0°. The mixture was extracted with 2N Na_2CO_3, and the acidified aqueous layer was repeatedly extracted with Et_2O. Evaporation of the dried ($MgSO_4$) extract afforded 0·35 g of acidic material, part of which (70 mg) was heated at 150°/15 mm in a sublimating apparatus. Some oil distilled, which was heated with water to convert the anhydride into the free acid. The presence of 2-isopropyl-2-methyl succinic acid (**7**) was detected in this product by TLC. [Silica gel F_{254} Merck; eluants, (a) benzene-MeOH-AcOH 45:8:4, (b) benzene-dioxane-AcOH 90:25:4; developer, bromocresol green in H_2O at pH 10]. Spots having the same R_f as **7** were obtained: (a), 0·52, (b), 0·415.

The rest of the initial acidic material was esterified with CH_2N_2 and chromatographed over neutral SiO_2 (Woelm, 80 g, 45 × 1·8 cm column), using as eluants pet ether, pet ether-benzene (1:1), benzene and benzene-Et_2O (1:1). The eluates were analyzed by GLC (columns, 1% NPGS on Chromosorb W 80–100 mesh, column temp 100°, injection block temp 140°, carrier gas N_2, flow rate 55 ml/min). The benzene-Et_2O fractions contained dimethyl 2-isopropyl-2-methylsuccinate in addition to 30% of an unidentified material. The mass spectrum of this mixture showed the same fragmentation pattern as an authentic sample of dimethyl 2-isopropyl-2-methylsuccinate in addition to some extraneous peaks.

A reference sample of **7** was prepared by the general method of Smith and Horwitz.[7] From 50 mmole

each of ethyl cyanoacetate, methyl isopropyl ketone and KCN, 20 mmole of 7 was obtained, m.p. 145–146° (from EtOAc-light petroleum); lit.[15] m.p. 148–149°.

22,29,30-*Trisnor*-17α-*isopropyl-A'-neogammaceran*-21α-*ol* (**15a**). The ketone **3a** (50 mg) in Et_2O (30 ml) was refluxed 2 hr with LAH (80 mg). Treatment with AcOEt, H_2O, filtration, evaporation and crystallization from $CHCl_3$–MeOH gave **15a**, m.p. 281–285°, $[\alpha]_D$ + 51°. (Found: C, 84·00; H, 12·37; $C_{30}H_{52}O$ requires: C, 84·04; H, 12·23%). This compound (12 mg) was treated with 0·5 ml of a 0·33 M soln of α-phenylbutyric anhydride in pyridine and left at room temp for 16 hr. After addition of two drops of H_2O and heating on a steam-bath for 30 min, H_2O (2 ml), excess 2N NaOH and benzene (3 ml) were added and the soln was extracted 3 times with benzene. The aqueous layer was acidified with 2N HCl and extracted with benzene; the organic layer, when concentrated to 2 ml, had α_D − 0·020° ± 0·002°.

Conversion of **15a** *into A'-neogammacer*-17(21)-*ene* (**16a**). A soln of **15a** (45 mg) in pyridine (3 ml) was treated with $POCl_3$ (0·3 ml), heated 2·5 hr at 100°, diluted with H_2O and extracted with pet ether. Filtration of the washed (2N HCl) and dried ($MgSO_4$) extract through Al_2O_3 gave 30 mg of olefinic material which was crystallized from Me_2CO to give pure **16a**, m.p. 176–179°, $[\alpha]_D$ + 47·2°.

20-*Benzylidene*-22,29,30-*trisnor*-17α-*isopropyl-A'-neogammaceran*-21-*one* (**13a**). A soln of **3a** (170 mg) and benzaldehyde (0·5 ml) in benzene (12 ml) and EtOH (22 ml) was treated with 1N KOH in EtOH (5 ml) and left at room temp for 85 hr. Crystals (140 mg) separated from the soln, while 15 mg more were obtained on concentration. Crystallization of the combined products from $CHCl_3$-MeOH gave **13a** (130 mg), m.p. 310–312°, $[\alpha]_D$ − 1·4°. (Found: C, 86·45; H, 10·53; $C_{37}H_{54}O$ requires: C, 86·32; H, 10·57%).

22,29,30-*Trisnor*-17α-*isopropyl*-20,21-*seco-A'-neogammacerane*-20,21-*dioic acid anhydride* (**14a**). Ozonized O_2 was bubbled at room temp for 30 min through a soln of **13a** (120 mg) in dry ($CaCl_2$) $CHCl_3$ (8 ml). After addition of H_2O (2 ml) and evaporation the residue was taken up in Et_2O, washed with 2N Na_2CO_3, dried, evaporated again and crystallized from hexane to give **14a** (55 mg), m.p. 265–268°, $[\alpha]_D$ + 33°, λ_{CO} 5·58, 5·71 μ. (Found: C, 78·63; H, 10·62; $C_{30}H_{48}O_3$ requires: C, 78·89; H, 10·59%).

α-Apoallobetulin series

19β,28-*Epoxy-A-neo*-18α-*olean*-3(5)-*ene* (α-*apoallobetulin*, **16b**) was prepared by the action of fuller's earth on betulin.[5] Since crystallization from $CHCl_3$-MeOH gave a product which still had a carbonylic impurity (IR), it was chromatographed through a 2 × 30 cm column of Al_2O_3. Pet ether containing 5% Et_2O (500 ml) eluted **16b**, which was crystallized from $CHCl_3$-MeOH, m.p. 209–213°, $[\alpha]_D$ + 79·5°. (Lit.[5] m.p. 200–201°, $[\alpha]_D$ + 74·7°). (Found: C, 84·83; H, 11·33. Calc. for $C_{30}H_{48}O$: C, 84·84; H, 11·39%).

19β,28:3,5α-*Diepoxy-A-neo*-18α-*oleanane* (**1b**). Treatment of **16b** (0·80 g) in $CHCl_3$ (40 ml) with 98% *p*-nitroperoxybenzoic acid (0·42 g) for 1 hr at 0°, followed by usual work-up and crystallization from $CHCl_3$-MeOH gave **1b**, m.p. 246–248°, $[\alpha]_D$ + 74·6°. (Found: C, 81·44; H, 10·89; $C_{30}H_{48}O_2$ requires: C, 81·76; H, 10·98%).

19β,28-*Epoxy*-A-*neo*-18α-*oleana*-3(5),6-*diene* (**2b**). A soln of **1b** (100 mg) in EtOH (50 ml) and conc HCl (5 ml) was refluxed 90 min, then diluted with H_2O and extracted with pet ether. Evaporation of the washed (2N NaOH) and dried ($MgSO_4$) extract, followed by crystallization from $CHCl_3$–MeOH gave **2b** (65 mg), m.p. 196–199°, $[\alpha]_D$ + 94°; λ_{max} 245 (infl), 252, 260 (infl) nm (ε 20,400, 23,500, 16,100); NMR, 2 olefinic H (AB part of an ABX system, centered at δ 5·90 ppm, J_{AB} 10·5 Hz). (Found: C, 85·09; H, 10·85; $C_{30}H_{46}O$ requires: C, 85·24; H, 10·97%).

19β,28-*Epoxy*-25-*nor*-3β-*methyl-A-neo*-18α-*oleana*-5(10),9(11)-*diene* (**3b**) and 19β,28-*epoxy*-4,23,24-*trisnor*-5β-*isopropyl-A-neo*-18α-*oleanan*-3-*one* (**4b**). A soln of **1b** (0·48 g) in $CHCl_3$ (24 ml) was treated with $BF_3 \cdot Et_2O$ (2·4 ml), left 3 hr at room temp, then washed with 2N Na_2CO_3, dried ($MgSO_4$) and evaporated. The residue was chromatographed through Al_2O_3; elution with pet ether containing 5% Et_2O gave the diene **3b** (0·38 g), m.p. 205–208° (from $CHCl_3$–MeOH), $[\alpha]_D$ + 127°; λ_{max} 237, 246, 255 nm (ε 22,000, 25,800, 16,900); NMR, one olefinic H at δ 5·25 ppm. (Found: C, 85·40; H, 11·23; $C_{30}H_{46}O$ requires: C, 85·24; H, 10·97%).

Further elution with Et_2O gave ketone **4b** (70 mg), m.p. 248–251°, $[\alpha]_D$ + 116°, λ_{CO} 5·79 μ, CD, $\Delta\varepsilon_{325}$ + 0·74, $\Delta\varepsilon_{313}$ + 1·25, $\Delta\varepsilon_{304}$ + 1·16 (Found: C, 81·55; H, 10·82; $C_{30}H_{48}O_2$ requires: C, 81·76; H, 10·98%).

19β,28-*Epoxy*-4,23,24-*trisnor*-5β-*isopropyl-A-neo*-18α-*oleanan*-3β-*ol* (**15b**). The ketone **3b** (80 mg) in anhyd Et_2O (30 ml) was refluxed 4 hr with LAH (170 mg). Usual work-up and crystallization from $CHCl_3$–MeOH afforded **15b** (45 mg), m.p. 218–221°, $[\alpha]_D$ + 75·3°. (Found: C, 80·98; H, 11·47; $C_{30}H_{50}O_2$ requires: C, 81·39; H, 11·38%).

This compound (35 mg) in pyridine (3 ml) was treated with $POCl_3$ (0·3 ml) and heated for 2·5 hr at

100°. Dilution with H_2O, extraction with pet ether and filtration of the washed (2N HCl) extract over Al_2O_3 afforded **16b** (25 mg), m.p. 209–212°, $[\alpha]_D$ + 79°.

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