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SOME NEW TRITERPENOIDS FROM LEAVES OF BETULA COSTATA TRAUTV.

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In investigating the unsaponifiable fraction of the ether extract from leaves of Betula costata Trautv., we isolated triterpenes A, B, C and D.

Triterpene A (I), $C_{30}H_{52}O_3$, m.p. 140-142°C (petroleum ether), $[\alpha]_D^{20}$ +4.80 (c 0.5; $CHCl_3$), hydroxyl absorption in the IR spectrum ($CHCl_3$) was observed at 3560 and 3620 cm^{-1}. Proton signals of eight tertiary methyl groups were detected in the PMR spectrum at δ (p.p.m.): 0.77 (3H, s), 0.88 (3H, s), 0.90 (3H, s), 1.0 (3H, s), 1.11 (3H, s), 1.57 (3H, s), 1.63 (3H, s); a vinylic proton signal was also detected at C-24, 5.09 (1H, t) along with a proton signal at C-3, 3.32 (1H, t, $J<4$ Hz). The value of the constant $J<4$ Hz is indicative of an α-configuration of the OH group at C-3.

In the ^{13}C-NMR spectrum of I, three carbon atom signals associated with the oxygen function of δ (p.p.m.) were observed: 76.3 (C-3), 78.9 (C-20), and 85.0 (C-17).*[1-3]

The mass spectrum of I contained peaks of the molecular ion M^+ 460 and of the tetracyclic fragment with m/e 333 ($M-C_8H_{15}O$).

The absence of a hydroxyl at C-12 causes the appearance of intensive side chain peaks with m/e 128 and m/e 110, resulting from disruption of the bond between fully substituted C-17 and C-20 atoms.

For priterpene A (I) isolated de novo, the structure dammar-24-ene, 3α, 17α, 20-triol has been suggested.

Triterpene B (II), $C_{30}H_{52}O_3$, m.p. 197-198° (acetone) was identified with betulafolienetriol according to physico-chemical constants and by comparison with an authentic sample. **

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* Here and further on, signals in ^{13}C-NMR spectra were assigned on the basis of model compounds and their derivatives, and also by means of selective and off-resonance decoupling.

**Betulafolienetriol samples were kindly provided by Dr. N. Seiler and Dr. S. Ichikawa.

Triterpene C (III), $C_{30}H_{52}O_5$, m.p. 250-251.5°, $[\alpha]_D^{20}$ + 6.0 (c 0.5; $CHCl_3$); hydroxylic absorption was observed in the IR spectrum ($CHCl_3$) at 3420 cm^{-1} (irrespective of concentration) and 3610 cm^{-1} (free OH). In the PMR spectrum of III, proton signals of eight tertiary methyl groups were observed at δ (p.p.m.): 0.83 (3H, s), 0.86 (3H, s), 0.93 (3H, s), 0.97 (3H, s), 1.11 (3H, s), 1.18 (3H, s), 1.29 (3H, s), 1.34 (3H, s); proton signals were also observed at carbon atoms with oxygen functions of δ (p.p.m.): 3.39 (1H, t, J=2.2 Hz) and 3.80 (1H, sex., J=11 Hz, J=7 Hz) at C-3 and C-12, respectively. The signal 3.74 (1H, t; J=6.6 Hz) belongs to the proton at C-24.

In the ^{13}C-NMR spectrum of III, we observed six carbon atom signals associated with the oxygen function of δ (p.p.m.): 67.7 (C-12), 70.1 (C-25), 76.2 (C-3), 85.5 (C-17), 85.7 (C-24), 89.5 (C-20).

Peaks with m/e 143 (100%), corresponding to the side chain fragment ($C_8H_{15}O_2$), and with m/e 59 $\left[(CH_3)_2\overset{+}{C}OH\right]$ were observed in the mass spectrum of III. This permitted us to determine the side chain of III as a substituted tetrahydrofurane cycle [4,5]. Four hydroxyls are contained in the molecule of III; two of them at C-3 and C-12 readily etherify, while the third hydroxyl-tertiary one contained in the side chain at C-25 acetylates under more drastic conditions[4].

Hydroxylic absorption in the IR spectrum ($CHCl_3$) of triacetate B (IV) was also observed at 3540 cm^{-1}. In oxidizing III with Jones' reagent in acetone[5], we obtained trisnoroxydiketolactone (V) with the same characteristics as the oxydiketolactone obtained by Fischer and Seiler from betulafolienetetraol[6].

Triterpene C, a new compound, has been named by analogy with betulafolienetriol oxide, an oxide of betulafolienetetraol[7].

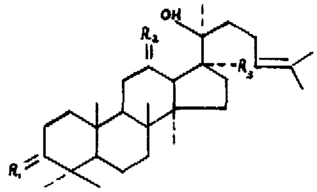
Triterpene D (VI), $C_{30}H_{52}O_4$, m.p. 168-170° (acetone), $[\alpha]_D^{20}$+ 8.50 (c 0.5; $CHCl_3$), in respect to physico-chemical properties corresponds to the previously isolated betulafolienetetraol[6].

Structure VI was also corroborated by a spectroscopic study. In the IR spectrum of VI ($CDCl_3$), we observed hydroxylic absorption at 3615 and 3370 cm^{-1}. In the PMR spectrum of VI (CHCl$_3$), eight signals of tertiary methyl groups showed at δ (p.p.m.): 0.84 (3H, s), 0.89 (3H, s), 0.95 (3H, s), 0.98 (3H, s), 1.18 (3H, s), 1.21 (3H, s), 1.63 (3H, s), 1.70 (3H, s). The above PMR spectrum also showed proton signals at carbon atoms with oxygen functions of δ (p.p.m.): 3.40 (1H, t) and 3.85 (1H, sex.), corresponding to the protons at C-3 and C-12; a vinylic proton signal on C-24 at 5.12 (1H, t) was also observed.

Peaks of M^+ 476, tetracyclic fragment with m/e 349 and m/e 376 (M^+ 100) were observed in the mass spectrum of VI.

Trisnoroxydiketolactone (V) forms on oxidizing VI with the Jones reagent; the action of perbenzoic acid on (VI)^5 resulted in two substances, one of which is identical to III. The other substance (IIIa) has the same general formula ($C_{30}H_{52}O_5$) and fragmentation in the mass spectrum similar to III.

The IR and PMR spectra of IIIa essentially differed from those of III. Oxidation of IIIa with Jones' reagent led to the formation of trisnoroxydiketolactone (V). Thus, IIIa may be considered to be the epimer of III on C-24.



I: $R_1 = {<}^{\cdot\cdot\mathrm{OH}}_{\mathrm{H}}$

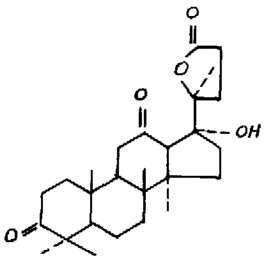
$R_2 = H_2$

$R_3 = {-}{-}\mathrm{OH}$

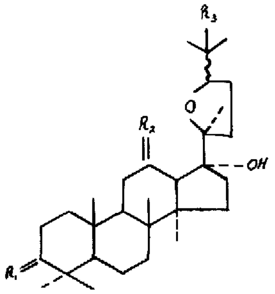
II: $R_1 = {<}^{\cdot\cdot\mathrm{OH}}_{\mathrm{H}}$; $R_2 = {<}^{\mathrm{OH}}_{\cdot\cdot\mathrm{H}}$; $R_3 = H_2$;

YI: $R_1 = {<}^{\mathrm{OH}}_{\mathrm{H}}$; $R_2 = {<}^{\mathrm{OH}}_{\cdot\cdot\mathrm{H}}$;

$R_3 = {-}{-}\mathrm{OH}$



Y



III: $R_1 = {<}^{\cdot\cdot\mathrm{OH}}_{\mathrm{H}}$; $R_3 = \text{—OH}$;

$R_2 = {<}^{\mathrm{OH}}_{\cdot\cdot\mathrm{H}}$;

IY: $R_1 = {<}^{\cdot\cdot\mathrm{OAc}}_{\mathrm{H}}$;

$R_2 = {<}^{\cdot\cdot\mathrm{OAc}}_{\cdot\cdot\mathrm{H}}$;

$R_3 = \text{—OAc}$;

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REFERENCES

1. F. Khuong-Huu, M. Sangare, V.M. Chari, A. Bekaert, M. Devys, M. Barbier and G. Lukacs, *Tetrahedron Letters*, 1787 (1975).
2. S. Seo, Y. Tomita and K. Tori, *J.C.S. Chem. Comm.*, 954 (1975).
3. L. Radics, M. Kajtar-Peredy, S. Corsano and L. Standoli, *Tetrahedron Letters*, 4287 (1975).
4. R. Tscheshe, G. Biernoth and G. Snatzke, *Ann. der Chemie*, 674, 196 (1964).
5. M. Nagai, N. Tanaka, O. Tanaka and S. Ichikawa, *Chem. Pharm. Bull.*, 21 2061 (1973).
6. F.G. Fischer and N. Seiler, *Ann. der Chemie*, 644, 146 (1961).
7. N.I. Uvarova, G.V. Malinovskaya, V.V. Isakov, A.K. Dzizenko, Yu. N. Elkin and G.B. Elyakov, Khim. Prirod. Soedinen., 659 (1975) (in Russian).