NEW TRITERPENES FROM THE LEAVES OF BETULA PENDULA AND BETULA ERMANII

N. D. Pokhilo, V. A. Denisenko,
and N. I. Uvarova

UDC 581.192+547.914

Continuing a study of the chemical composition of the leaves of one of the birch species most widely distributed in the Soviet Union (Betula pendula Roth. [1]) we have analyzed the unsaponifiable part of an ethereal extract of leaves gathered in June, 1985, in the environs of Minsk. The following triterpenoids have been isolated and identified (% on the weight of the air-dry leaves): betulafolienetriol) 0.09; dammar-24-ene-3α,12β,17α,20(S)-tetraol) 0.08; betulafolienetriol oxide) 0.015; dammar-24-ene-3α,17α,20(S)-triol) 0.01; dammar-25-ene-3α,12β,17α,20(S),24(ξ)-pentaol) 0.03 [1]; and a triterpene (I) with mp 278-280°C (acetone) not previously isolated from plant materials.

The IR spectrum of (I) showed the presence of hydroxy groups (3610, 3567, 3338 cm^{-1}). The PMR spectrum of (I) ($CDCl_3$, 250 MHz, ppm) contained in the strong field the signals of the protons of eight tert-Me groups in the 0.84-1.34 ppm region, and in the weak field the signals of protons at 3.40 (1H, t, J = 3 Hz, H-3e); 3.72 (1H, m, Σ J = 30 Hz, H-12a); 3.90 (1H, dd, J = 5 Hz, J = 10 Hz, H-24); 5.44 (1H, d, J = 3 Hz, —OH). ^{13}C NMR spectrum ($CDCl_3$, 62.9 MHz, ppm): 33.7 (C-1); 25.5 (C-2); 76.0 (C-3); 37.6 (C-4); 49.5 (C-5); 18.3 (C-6); 34.3 (C-7); 40.6 (C-8); 50.3 (C-9); 37.4 (C-10); 32.6 (C-11); 67.1 (C-12); 51.6 (C-13); 51.3 (C-14); 33.4 (C-15); 38.0 (C-16); 85.5 (C-17); 16.2 (C-18); 15.9 (C-19); 91.2 (C-20); 23.3 (C-21); 34.2 (C-22); 25.5 (C-23); 88.4 (C-24); 70.2 (C-25); 27.6 (C-26); 24.3 (C-27); 28.3 (C-28); 22.1 (C-29); 18.4 (C-30). A comparison of the ^{13}C chemical shifts (CSs) of compounds of the 20(S),24(R)-epoxydammarane series and their 20(S),24(S)-analogues showed that for the 24(S)-analogues the value of the C-24 CS was 87.4-88.4 ppm, while in the case of the 24(R)- configuration it was 84.1-85.6 ppm [2, 3]. This permitted the assumption that compound (I) had the structure of 20(S),24(S)-epoxydammarane-3α,12β,17α,25-tetraol.

The oxidation of dammar-24-ene-3α,12β,17α,20(S)-tetraol with perbenzoic acid has been described [4]. It led to two compounds, one of which was identical with 20(S),24(R)-epoxydammarane-3α,12β,17α,25-tetraol, while the second substance could apparently be considered as its epimer at C-24. This second compound gave no depression of the melting point with the triterpene (I). The difference in the PMR details for (I) given in the present communication and for the identical compound published by us previously [4] is due to an erroneous assignment in [4] of the signals for the H-12 and H-24 protons, which should be interchanged.

Thus, the structure of (I) may be defined unambiguously as 20(S),24(S)-epoxydammarane-3α,12β,17α,25-tetraol.

We have previously studied the unsaponifiable part of an ethereal extract of the leaves of Betula ermanii Cham. growing on Kamchatka, and from it were isolated 20(S),24(R)-epoxydammarane-3β,11α,25-triol (II) and its acetate at C-11 (III) [5]. In B. ermanii leaves gathered in June, 1988, in the environs of the village of Kuril'sk (island of Iturup), in addition to the triterpene (II), we detected another triterpene alcohol (IV) which it was possible to isolate only in the form of the crystalline diacetate (V), $[\alpha]_{578}^{3}$ +71.2° (c 0.5; $CHCl_3$), after the acetylation of the corresponding fraction followed by chromatographic separation of the mixture.

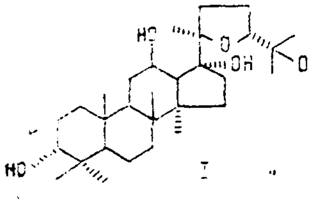
In the IR spectrum of (V), absorption bands were observed at 3684 and 3604 cm^{-1} (OH group) and at 1724 cm^{-1} (ester group). PMR spectrum of (V), ($CDCl_3$, 250 MHz, ppm): 0.86, 0.87, 0.94, 0.99, 1.00, 1.13, 1.62, 1.69 (3 H, s) [the protons of tert-Me groups; 1.97, 2.05 (3 H, s)] the protons of acetate groups: 4.46 (1H, dd, J = 8 Hz, J = 10 Hz, H-3a); 5.12 (1H, m, ΣJ = 18 Hz, H-24); 5.22 (1H, α , J = 6 Hz, J = 10 Hz, H-11a). ^{13}C NMR spectrum

---

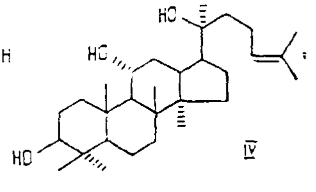
Pacific Ocean Institute of Bioorganic Chemistry, Far-Eastern Branch, Academy of Sciences of the USSR, Vladivostok. Translated from Khimiya Prirodnykh Soedinenii, No. 1, pp. 145-146, January-February, 1991. Original article submitted March 11, 1990; revision submitted June 25, 1990.

($CDCl_3$, 62.9 Mhz, ppm): 39.1 (C-1), 23.9 (C-2); 80.3 (C-3); 38.3 (C-4); 55.8 (C-5); 18.1 (C-6); 35.7 (C-7); 41.0 (C-8); 52.8 (C-9); 38.7 (C-10); 72.6 (C-11); 34.8 (C-12); 39.1 (C-13); 50.0 (C-14); 30.7 (C-15); 24.9 (C-16); 49.9 (C-17); 16.9 (C-18); 16.2 (C-19); 74.7 (C-20); 25.6 (C-21); 40.4 (C-22); 22.6 (C-23); 124.5 (C-24); 131.5 (C-25); 25.6 (C-26); 17.6 (C-27); 28.2 (C-28); 16.4 (C-29); 16.9 (C-30); acetate C's: 21.9; 21.2; 170.5; 169.8. By comparing the PMR and ^{13}C NMR spectra of (V) with the corresponding spectra of (II) and (III) [5] and also those of dammar-24-ene-3α,12β,17α,20(S)-tetraol [3], triterpene (V) was ascribed the structure of 3β,11α-diacetoxydammar-24-en-20(S)-ol.

Consequently, the initial alcohol had the structure of dammar-24-ene-3β,11α,20(S)-triol. This compound has not previously been isolated from natural sources.



I



IV

LITERATURE CITED

1. N. D. Pokhilo, V. A. Denisenko, V. V. Makhan'kov, and N. I. Uvarova, Khim. Prir. Soedin., 179 (1986).
2. O. Tanaka and S. Yahara, Phytochemistry, 17, 1353 (1978).
3. V. A. Denisenko, V. L. Novikov, G. V. Malinovskaya, and G. B. Elyakov, Izv. Akad. Nauk SSSR, Ser. Khim., 2727 (1983).
4. N. I. Uvarova, G. V. Malinovskaya, Yu. N. El'kin, V. V. Isakov, A. K. Dzizenko, and G. B. Elyakov, Khim. Prir. Soedin., 757 (1976).
5. G. B. Malinovskaya, N. D. Pokhilo, V. V. Isakov, and N. I. Uvarova, Khim. Prir. Soedin., 587 (1978); V. L. Novikov, G. V. Malinovskaya, N. D. Pokhilo, and N. I. Uvarova, Khim. Prir. Soedin., 50 (1980).