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LETTERS TO THE EDITOR

Synthesis of Optically Active *O,O*-Di-*L*-(–)- and *O,O*-Di-*D*-(+)-menthyldithiophosphoric Acids and Their Ammonium Salts

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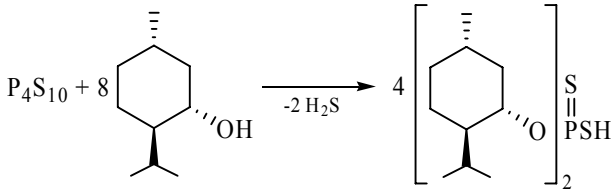
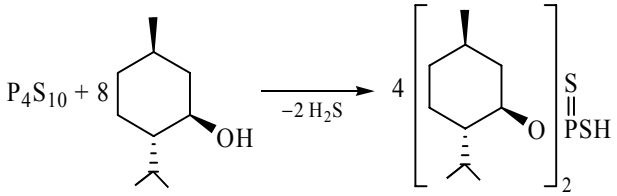
Aiming to obtain new biologically active compounds, we undertook studies of thiophosphorylation of organic substances of natural origin of terpenoid series by the example of reaction of *O,O*-diisopropyldithiophosphoric acid with (+)-limonene [1]. In the present work we have chosen as the new thiophosphorylation objects such terpene alcohols as *L*- and *D*-menthols containing asymmetric carbon atoms and displaying optical activity. Tetraphosphorus decasulfide have been used earlier to determine enantiomeric and diasteromeric excess of alcohols containing chiral centers [2, 3]. However, the reaction of *L*-menthol with tetraphosphorus decasulfide was examined only by ^{31}P NMR spectroscopy method without isolation and identification of the product [3]. In this connection we performed a more complete identification of the product of the reaction of tetraphosphorus decasulfide **I** with *L*-(–)-menthol **IIa** at the molar ratio 8:1 in chloroform at 50°C for 2 h.



I **IIb** **IIIb**

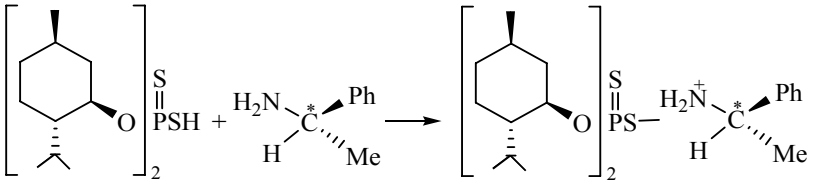
O,O-Di-*L*-(–)-menthyldithiophosphoric acid **IIIa** shows optical activity: $[\alpha]_D^{22}$ –64.7° (*c* 1.0, C_6H_6) in agreement with an optical rotatory angle sign of the initial alcohol **Ia** {(4]: $[\alpha]_D^{23}$ –48°, *c* 10, EtOH). It was established that isomeric *O,O*-di-*D*-(+)-menthyldithiophosphoric acid **IIIb** forming at the heating of phosphorus sulfide **I** with *D*-(+)-menthol **IIb** under similar conditions also retains the sign of the optical rotatory angle ($[\alpha]_D^{22}$ +65.8°, *c* 1.0, C_6H_6) of starting alcohol **IIb** ([4]: $[\alpha]_D^{23}$ +48°, *c* 10, EtOH).



I **IIa** **IIIa**

The IR, ^{31}P and ^{1}H NMR and mass spectral parameters of isomeric dithiophosphoric acids **IIIa** and **IIIb** are identical. Dithiophosphoric acids **III** were transformed into the corresponding ammonium salts among which compounds obtained from the chiral amines [for example, *L*-(–)-α-methylbenzylamine **IV**] are of an essential interest. *L*-(–)-α-Methylbenzylammonium salt of *O,O*-di-*L*-(–)-menthyldithiophosphoric acid **V** obtained by the treating of dithiophosphoric acid **IIIa** with amine **IV** retains optical activity ($[\alpha]_D^{22}$ –60.0°, *c* 1.0, C_6H_6).

***O,O*-Di-*L*-(–)-menthyldithiophosphoric acid (IIIa).** To a solution of 10.0 g of alcohol **IIa** in 60 ml of anhydrous $CHCl_3$ was added by portions 3.5 g of



IIIa **IV** **V**

phosphorus sulfide **I** at 20°C in the dry argon flow under stirring. This mixture was heated at 50°C for 2 h under stirring. After cooling the mixture was filtered and concentrated for 1 h (0.5 mm Hg) at 40°C and for 1 h (0.02 mm Hg) at 40°C. Yield 11.5 g (88%). IR spectrum, ν, cm^{-1}: 2406 w.br [ν(S–H)]; 2955 s, 2924 s, 2854 s [$\nu_{as,s}(CH_3)$, $\nu_{as,s}(CH_2)$]; 1458 s [$\delta_{as}(CH_3)$]; 1377 m [$\delta_s(CH_3)$]; 1023 m, 985 m, 963 m.br [ν(P–O–C)], [ν(O–C)]; 675 m [ν(P=S)]; 548 w [ν(P–S)]. ^{1}H NMR spectrum, δ, ppm: 0.83 d and 0.86 d (3H×2, C*H*$_3$CH, $^3J_{HH}$ 8.8 Hz); 0.94 d and 0.95 d (6H×2, (C*H*$_3$)$_2$CH, $^3J_{HH}$ 6.6 Hz); 1.15 m [1H×2, (CH$_3$)$_2$C*H*–CH); 1.43 m (1H×2, CH$_3$C*H* cycl.); 1.69 m (2H×2, CH$_3$CH·C*H*$_2$CH$_2$); 1.99 d (1H×2, POCHCH*H-a*, $^3J_{HH}$ 11.7 Hz); 2.09–2.21 m (2H×2, POCHCHC*H*$_2$); 2.38 d (1H×2, POCHCH*H-e*, $^3J_{HH}$ 11.7 Hz); 3.44 d.t (1H×2, POCHC*H*-cycl., $^3J_{HH}$ 6.6 Hz); 4.46 d.d.t (1H×2, POC*H*-cycl., $^3J_{HH}$ 6.6 Hz, $^3J_{PH}$ 11.0 Hz). ^{31}P NMR spec-trum, δ_P, ppm: 81.9. Mass spectrum (EI), *m/z*: 406 $[M]^{+\cdot}$. Found, %: C 59.36; H 9.76; P 7.48; S 15.63. $C_{20}H_{39}O_2PS_2$. Calculated, %: C 59.09; H 9.67; P 7.62; S 15.77. Mr 406.6.

***O,O*-Di-*D*-(+)-menthyldithiophosphoric acid (IIIb).** Yield 88%. Found, %: C 59.36; H 9.56; P 7.25; S 15.48. $C_{20}H_{39}O_2PS_2$. Calculated, %: C 59.07; H 9.67; P 7.62; S 15.77.

***L*-(–)-α-Methylbenzylammonium salt of *O,O*-di-*L*-(–)-menthyldithiophosphoric acid (V).** To a solution of 3.2 g of acid **IIIa** in 10 ml of anhydrous benzene was added dropwise a solution of 0.95 g of amine **IV** in 10 ml of benzene at 20°C in the dry argon flow under stirring. This mixture was stirred for 1 h at 20°C, then kept for 12 h at 20°C and concentrated for 1 h under vacuum (0.5 mm Hg) at 40°C and for 1 h (0.02 mm Hg) at 40°C. Yield 2.9 g (70%). IR spectrum, ν, cm^{-1}: 3345 w.br [$\nu_{free}(NH_3^+)$]; 3273 w [$\nu_{bonded}(NH_3^+)$]; 2954 s, 2974 s, 2868 s [$\nu_{as,s}(CH_3)$, $\nu_{as,s}(CH_2)$, CH]; 1589 m, 1495 m [ν(C=C, Ar)]; 1453 s [$\delta_{as}(CH_3)$]; 1389 m, 1370 m [$\delta_s(CH_3)_2C_{gem}$]; 1021 s [ν(P–O–C)]; 978 s.br [ν(O–C)]; 670 s [ν(P=S)]; 576 m [ν(P–S)]. ^{1}H NMR spectrum, δ, ppm: 0.79 d, 0.80 d, 0.81 d and 0.84 d (6H×2, C*H*$_3$CH-cycl., $^3J_{HH}$ 7.0 Hz); 0.88 d, 0.89 d, 0.895 d and 0.90 d [12H, (C*H*$_3$)$_2$CH, $^3J_{HH}$ 7.0 Hz]; 0.98–1.11 br.s (C*H*); 1.27 m (C*H*); 1.40 m (C*H*); 1.50 d (3H, C*H*$_3$CHN, $^3J_{HH}$ 6.7 Hz); 1.63 m (C*H*$_2$); 1.94 m (C*H*); 2.17 m and 2.34 m (C*H*$_2$, $^3J_{HH}$ 7.0 Hz); 3.40 d.d.t (1H×2, POCHC*H*-cycl., $^3J_{HH}$ 6.0 Hz); 4.02 m (1H, NC*H*); 4.20–4.30 m (1H×2, POC*H*-cycl., $^3J_{HH}$ 7.0 Hz); 7.26–7.38 m (5H, C$_6$*H*$_5$). ^{31}P NMR spectrum (C$_6$H$_6$), δ_P, ppm: 106.6. Mass spectrum (EI), *m/z*: 527 $[M]^+$. Found, %: C 63.82; H 9.43; N 2.99; P 5.68; S 12.43. $C_{28}H_{50}NO_2P$. Calculated, %: C 63.72; H 9.55; N 2.65; P 5.87; S 12.15. M 527.8

The IR spectra were recorded on a Bruker Vector 22 IR Fourier-spectrometer (KBr). The ^{1}H NMR spectra were taken on an Avance-600 spectrometer (600 MHz) in $CDCl_3$; the ^{31}P NMR spectra, on a Bruker CXP-100 spectrometer (36.5 MHz) relative to external reference (85% H_3PO_4) in $CHCl_3$. The mass spectra were registered on a TRACE MS Finnigan MAT mass-spectrometer (70 eV).

REFERENCES

1. Nizamov, I.S., Sofronov, A.V., Nizamov, I.D., Cherkasov, R.A., and Nikitina, L.E., *Zh. Obshch. Khim.,* 2007, vol. 43, no. 4, p. 621.

2. Al'fonsov, V.A., Garifzyanova, G.G., Dimukhametov, M.N., and Bredikhin, A.A., *Zh. Obshch. Khim.,* 1998, vol. 68, no. 3, p. 517.

3. Feringa, B.L.J., *Chem. Soc., Chem. Commun.*, 1987, no. 9, p. 695.

4. *Aldrich. Catalog Handbook of Fine Chemicals*, Milwaukee, USA, 1994–1995, p. 933,