New flavonoid oligoside from *Aconitum barbatum* Pers.

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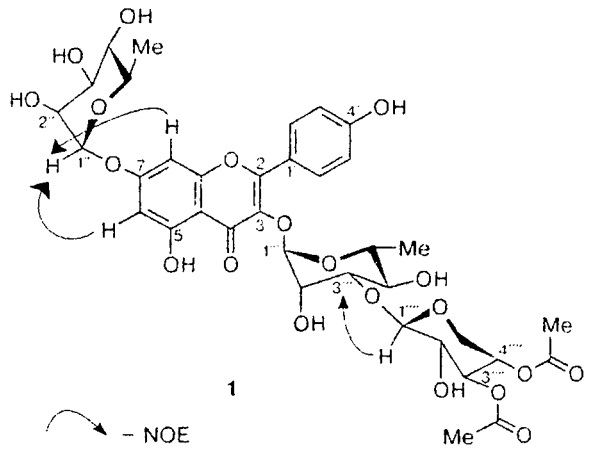
A new flavonoid oligoside, *viz.*, 3-*O*-[3,4-(di-*O*-acetyl-β-xylopyranosyl)-α-rhamnopyranosyl]-7-*O*-(α-rhamnopyranosyl)kaempferol, was isolated from the above-ground part of the plant *Aconitum barbatum* Pers. The product was identified by spectral methods.

Key words: *Aconitum barbatum*, flavonoids, glycosides, ^1H and ^{13}C NMR spectroscopy, FAB mass spectrometry.

The plant *Aconitum barbatum* Pers. (barbate wolfsbane) is used in Tibetan medicine for the treatment of contagious and gastroenteric diseases, nephritic, hepatic, and gastric colic, and skin parasitic diseases. This plant produces alkaloids and flavonoids.[1,2] It has been reported[2] that the flavonoid content amounts up to 1.2%. However, the chemical nature of these compounds has not previously been investigated. The present study closes this gap.

An individual compound with the molecular weight of 795 $[M + H]^+$, which we named barbaside A (**1**), was isolated by chromatography from the ethyl acetate fraction of the methanol extract obtained from the above-ground part of the plant.*

The UV spectra recorded in MeOH containing additives of ionizing and complex-forming reagents demonstrated that the compound under study contains a flavonoid fragment[3] whose free OH groups are located at positions 5 and 4′.



The IR spectrum of compound **1** has bands typical of stretching vibrations of the benzopyrone ring. In addition to the carbonyl group of the γ-pyrone ring (1654 cm^{-1}), the molecule contains two more carbonyl groups (1719 and 1735 cm^{-1}).

The ^1H NMR spectrum has signals for three anomeric protons at δ 5.63, 5.45, and 4.65, which indicates that the molecule contains three carbohydrate residues. The ^{13}C NMR spectrum demonstrates that compound **1** contains 36 carbon atoms 15 of which belong to the flavone moiety. Of the remaining carbon atoms, 12, 4, and 5 atoms belong to two deoxyhexose residues, two acetate groups, and the pentose moiety, respectively (Table 1).

The ^1H NMR spectrum has doublet signals for the H(6) and H(8) protons at δ 6.46 and 6.77, respectively. Consequently, the ring A contains substituents at positions 5 and 7. The presence of the OH group at the C(5) atom is evidenced by the signal for the proton at δ 12.3 in the ^1H NMR spectrum recorded in acetone-d_6. Two two-proton doublets at δ 7.78 and 7.03 belong to the pair H(2′) and H(6′) and the pair H(3′) and H(5′), respectively. This fact is confirmed by the UV spectral data, which are indicative of the presence of a substituent at position 4′ of the ring B.

In the flavone molecule, the saccharide residues are most probably attached to the carbon atoms at positions 3 and 7 because these atoms do not contain free hydroxy groups and are bound to the oxygen atoms. Glycosylation occurs at the O(3) position as evidenced by the absence of a characteristic singlet for the H(3) proton in the ^1H NMR spectrum and the presence of a signal (singlet) at δ 136.1 in the ^{13}C NMR spectrum, which can be assigned to the glycosylated C(3) atom. Glycosylation at the O(7) atom follows from the UV spectral data and the characteristic signals in the ^{13}C NMR spectrum belonging to the C(7), C(6), and C(8) atoms (see Table 1).[4]

The first information on the nature of the saccharide residues was obtained from analysis of the ^1H NMR

* The absolute configurations of the monosaccharide residues were not established; the L and D configurations of the rhamnose and xylose residues, respectively, are given.

Published in *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 11, pp. 1935–1937, November, 2000.

1066-5285/00/4911-1905 $25.00 © 2000 Kluwer Academic/Plenum Publishers

Table 1. Data of ^{13}C and ^{1}H NMR spectroscopy (acetone-d_6, δ, *J*/Hz) for compound **1**

Atom	δ ^{13}C	δ ^{1}H	NOE
C(2)	157.1	—	
C(3)	136.1	—	
C(4)	181.11; 180.90 (180.29; 180.28)**	—	
C(5)	161.2	—	
C(6)	99.5	6.46 (d, *J* = 2.5)	H(1″)—H(6)
C(7)	163.3	—	
C(8)	95.5	6.77 (d, *J* = 2.5)	H(1″)—H(8)
C(9)	159.1	—	
C(10)	107.3	—	
C(1′)	122.4	—	
C(2′)	131.8	7.87 (d, *J* = 8.5)	
C(3′)	116.7	7.03 (d, *J* = 8.5)	
C(4′)	162.9	—	
C(5′)	116.7	7.03	
C(6′)	131.8	7.87	
C(1″)	99.66	5.63 (s)	
C(2″)	71.39	4.05 (m)	
C(3″)	72.14	3.83 (dd, *J* = 2.5; *J* = 9.0)	H(3″)—H(5″)
C(4″)	73.64	3.53 (m) 3.56 (t, *J* = 9.4)**	
C(5″)	70.13	3.60 (m)	
C(6″)	18.2	1.22 (d, *J* = 6.1)	
C(1‴)	102.5	5.44 (s)	
C(2‴)	71.46	4.25 (br.s)	
C(3‴)	83.65	3.53 (dd, *J* = 2.0; *J* = 9.5) 3.50 (dd, *J* = 9.4)**	H(3‴)—H(5‴) H(3‴)—H(1⁗)
C(4‴)	73.41	3.53 (m) 3.51 (t, *J* = 9.4)**	
C(5‴)	69.77	3.40 (m)	
C(6‴)	18.0	0.97 (d, *J* = 6.1)	
C(1⁗)	106.13	4.65 (d, *J* = 7.6)	H(1⁗)—H(3‴) H(1⁗)—H(3⁗)—H(5⁗)
C(2⁗)	73.41	3.50 (m) 3.50 (d, *J* = 9.4)**	
C(3⁗)	75.37	5.08 (t, *J* = 9.5)	
C(4⁗)	70.84	4.78 (td, *J* = 5.5; *J* = 10.0)	
C(5⁗)	63.7	3.95 (dd, *J* = 5.5; *J* = 11.4) 3.43 (m)	
CH_3	20.83, 20.60	1.95, 2.00	
CO	172.60, 172.21		

* Integral intensities of the signals in the ^{1}H NMR spectra correspond to the expected values. The total integral intensity of two signals for the C(4) atom in the ^{13}C NMR spectrum corresponds to the intensity of the individual signal for the single carbon atom.
** In methanol-d_4.

spectra in which the singlet signals for the anomeric protons of rhamnose at δ 5.44 and 5.63 and the signals for the protons of the methyl groups of this monosaccharide at δ 1.22 and 0.97 were readily identified. Based on these signals and using the 2D TOCSY spectrum, we assigned the signals for the protons to the individual monosaccharide residues. The COSY experiment allowed us to make the following assignment of the protons in the carbohydrate residues: Rha-1: δ 5.63 → 4.05 → 3.83 → 3.53 → 3.60 → 1.22; Rha-2: δ 5.44 → 4.25 → 3.50 → 3.50 → 3.40 → 0.97. Taking into account these data, the spin-spin coupling constants for the nonoverlapping signals in the one-dimensional ^{1}H NMR spectrum were determined (see Table 1). The presence of cross-peaks for the protons H(3″)—H(5″) (Rha-1) and H(3‴)—H(5‴) (Rha-2) in the NOESY spectrum and the absence of NOE for H(1″)—H(5″) and H(1⁗)—H(5‴) are unambiguously indicative of the α-configurations of both rhamnopyranoside residues.

It is known[3] that the signal for the anomeric proton of rhamnose bound to the flavone molecule at position 7 is observed at lower field than those in the case of 3-*O*-rhamnosides. Consequently, Rha-2 and Rha-1 can be located at positions 3 and 7, respectively. Actually, the anomeric proton of Rha-1 has cross-peaks with the H(6) and H(8) protons in the NOESY spectrum, whereas the anomeric proton of Rha-2 does not give cross-peaks other than those with the protons of its own ring. The assignment of the signals for the carbon atoms in each of the rhamnose residues was made with the use of the HETCOR procedure (Table 1). The results for Rha-1 agree well with the published data[4] for 7-*O*-rhamnosyl derivatives of kaempferol. In the case of Rha-2, the signal for the C(3‴) atom is shifted downfield by 11.51 ppm compared to that observed for 3-*O*-rhamnoside of quercetin. Consequently, the third saccharide residue is bound to Rha-2 at position 3.

Based on the signal for the anomeric proton at δ 4.65, the signals for the protons of pentose and the relations between them were determined from the TOCSY and COSY spectra: δ 4.65 → 3.50 → 5.08 → 4.78 → (3.43 → 3.95). The assignment of the signals for the carbon atoms of this pentose moiety in the ^{13}C NMR spectrum was made using the HETCOR procedure (see Table 1). The observed chemical shifts of the carbon atoms of pentose and the spin-spin coupling constants for the H(1⁗), H(2⁗), H(3⁗), and H(5⁗) protons (see Table 1) in the ^{1}H NMR spectrum are similar to the corresponding values reported for β-xylopyranose.[6] The NOESY spectrum has cross-peaks, which are indicative of coupling between the anomeric proton of xylopyranose and the axial protons at the C(3‴) and C(5⁗) atoms with the chemical shifts of 5.08 and 3.43 ppm, respectively. This suggests that the glycoside bond of xylopyranose has the β configuration. The fact that the NOESY spectrum has cross-peak of the anomeric proton of xylose with the protons at the C(3‴) atom indicates that xylose is bound to Rha-2 at position 3. The chemical shifts of the H(3⁗) and H(4⁗) protons lie in the region of acylated hydroxymethine groups. Acylation of these groups is also confirmed by the fact that the signals for the H(2⁗) and H(5⁗) protons are shifted

upfield. Acetylation at position 4"" is also evidenced by the fact that the signal for the C(5"") atom is shifted upfield by 3.5 ppm compared to the signal for β-xylopyranose[7] in the ^{13}C NMR spectrum of compound **1**. No downfield shifts of the signals for the C(3"") and C(4"") atoms are observed due to the fact that the α-effect of acetylation is masked by the β-effect due to acetylation of the adjacent OH groups. All the above-considered data provide evidence that the compound under study, *viz.*, barbaside A, is 3-*O*-[3-*O*-(3,4-di-*O*-acetyl-β-xylopyranosyl)-α-rhamnopyranosyl]-7-*O*-(α-rhamnopyranosyl)kaempferol (**1**).

Experimental

The melting point was determined on a Kofler stage. The optical rotation was measured on a Polamat A polarimeter. The UV spectra were recorded on a Specord UV-VIS spectrophotometer. The IR spectra were measured on an IFS25 Fourier spectrometer. The ^1H and ^{13}C NMR spectra were recorded on a Varian VXR-500S instrument equipped with a SPARC SI+ computer with the standard VNMR software. The quantitative ^{13}C NMR spectrum was measured with pulse delay of 11 s. The NOESY spectrum was recorded on a Bruker DPX-400 instrument. The FAB mass spectra were obtained on a JEOL SX 102 instrument.

Column chromatography was performed with the use of silica gel Lachema L 40/70 μm. Thin-layer chromatography was carried out with the use of silica gel Lachema L 5/40 μm. The spots on chromatograms were visualized by spraying with a 5% ethanolic solution of $AlCl_3$ and with a 1% vanillin solution in 50% orthophosphoric acid.

The plant *Aconitum barbatum* Pers. was collected when it bloomed in the Shelekhovskii district of the Irkutsk region. Total flavonoids were isolated according to the following procedure. Finely divided and air-dried leaves and flowers (1.36 kg) were extracted with MeOH (9 L) at 20 °C. The extract was concentrated, water was added, and the mixture was extracted successively with $CHCl_3$ (0.7 L), AcOEt (0.6 L), and Bu^nOH (1 L). Individual compound **1** was isolated from the ethyl acetate fraction (1.5 g) by flash chromatography on a dry column.[8] Elution was carried out with the use of a $CHCl_3$—MeOH mixture with a gradual increase in the concentration of MeOH. TLC analysis of the fractions using a 35 : 23 : 2 $CHCl_3$—MeOH—H_2O system demonstrated that the fractions obtained by elution with a $CHCl_3$—MeOH mixture (80 : 20 and 76 : 24) contained predominantly compound **1**. Repeated chromatography of each of these fractions under analogous conditions afforded a purer substance whose recrystallization gave compound **1** in a yield of 12 mg.

3-*O*-[3-*O*-(3,4-Di-*O*-acetyl-β-xylopyranosyl)-α-rhamnopyranosyl]-7-*O*-(α-rhamnopyranosyl)kaempferol (1), m.p. 224 °C (EtOH), $[\alpha]_{546}^{20}$ −195° (*c* 0.53, EtOH). MS, *m/z*: 795 $[M + H]^+$; $C_{36}H_{42}O_{20}$. IR (KBr), ν/cm^{-1}: 3425 (OH), 1654 (C=O), 1600 (C=C), 1513, 1492, 838 (arom), 1719, 1735 (C=O of the acetate group). UV (MeOH), λ_{max}/nm (lg ε): 265 (4.34), 320 (4.10), 343 (4.16); +AcONa 266, 358, 400 sh; +AcONa +H_3BO_3 266, 318, 345; +MeONa 245, 273, 382; +$AlCl_3$ 235, 275, 301, 345, 400; +$AlCl_3$ +HCl 275, 301, 338, 396. The ^1H and ^{13}C NMR spectral data are given in Table 1.

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Received April 12, 2000;
in revised form July 12, 2000

Unusual macrocyclic diol from *Stellaria media* (L.) Vill.

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A new macrocyclic diol, mediaglycol, was isolated from the plant *Stellaria media* (L.) Vill. (Caryophyllaceae family). The compound was identified as 1-(1,2-dihydroxyethyl)-1-isopropylcyclononadecane based on spectral data.

Key words: *Stellaria media*, Caryophyllaceae, macrocyclic metabolites, NMR spectroscopy, 1-(1,2-dihydroxyethyl)-1-isopropylcyclononadecane.

The plant *Stellaria media* (Caryophyllaceae family, chickweed *S. media* Vill.) can be found throughout the whole temperate zone of the North hemisphere. It is widely used in traditional medicine as an antirheumatic, antiphlogistic, healing, and diuretic remedy and as a tonic.[1] The chemical composition of the plant has not been adequately studied. Flavonoids,[2] monoacylgalactolipids, ferulic acid,[3] lipids,[4,5] β-sitosterol and its glucoside,[5] and amino acids[6] have been isolated from the above-ground part of the plant.

The purpose of this work was to search for new secondary metabolites that might be responsible for the physiological action of extracts from *S. media*.

A colorless crystalline compound with the molecular formula $C_{24}H_{48}O_2$ was isolated by liquid—solid column chromatography from a hexane extract of the above-ground part of *S. media*. The elemental composition was determined using the data of elemental analysis, mass spectrometry and quantitative measurements in the ^{13}C and ^1H NMR spectra.

The electron impact mass spectrum exhibits a relatively intense molecular ion peak with *m/z* 368. Analysis of this spectrum provided grounds to suggest that the molecule contains a saturated hydrocarbon macrocycle.[7] Indeed, the ion peak with *m/z* 340 corresponded to a typical elimination of two carbon atoms as C_2H_4 from the molecular ion. The ions with *m/z* 153 $[C_{11}H_{21}]^+$ and 127 $[C_9H_{19}]^+$ show a fragmentation pattern typical of hydrocarbon fragments. The characteristic ion peaks comply with the formula C_nH_{2n-1}. The coefficient of hydrogen unsaturation indicated the presence of one ring in the molecule.

The structure of the substance was determined from the ^1H and ^{13}C NMR spectra (Table 1) recorded using the COSY and NOESY 2D techniques. The ^1H NMR spectrum ($CDCl_3$) contained signals for two magnetically equivalent methyl groups and for the proton of a methine group bound to them. The spin—spin coupling pattern (see Table 1) implied the presence of an isopropyl group attached to a quaternary carbon atom. The spectrum also exhibited resonance signals of the CH_2OH and CHOH groups linked to each other. The signal of the methine proton at 3.44 ppm was a doublet of doublets, due to the coupling with two magnetically nonequivalent protons of the hydroxymethyl group. This group was responsible for two poorly resolved multiplets at 3.64 and 3.71 ppm. When $CDCl_3$ was replaced by deuterated methanol, the signal of the methine proton shifted downfield to 3.64 ppm and appeared as a broad multiplet. In this solvent, the protons of the hydroxymethyl group accounted for two sharp doublets of doublets at 3.47 and 3.56 ppm with spin—spin coupling constants of 11.1, 6.6 and 11.1, 4.3 Hz. The 2D COSY spectrum indicated that the hydroxy groups belonged to an α-glycol group and the type of the spin—spin coupling of the methine proton (the spectrum in $CDCl_3$) attested that the methine group was attached to a quaternary C atom. Most of the ring carbon atoms accounted for one broad signal at about 29.70—29.96 ppm in the ^{13}C NMR spectrum. The use of the quat pulse sequence[8] showed that the molecule contains only one quaternary carbon atom responsible for a signal at 29.80 ppm and, hence, it is this atom that carries both the isopropyl and glycol fragments.

The ^1H NMR spectrum of the compound exhibited two more two-proton multiplets at 1.15 and 1.43 ppm, which were assigned to C(2) and C(19) methylene groups, and a broadened signal due to 32 protons at 1.24 ppm. The ^{13}C NMR and IR spectral data confirmed the presence of the isopropyl and glycol groups in the molecule. In the solvents used (CD_3OD and $CDCl_3$ stabilized by deuterioethanol), no signals for the protons of the hydroxy groups at C(1′) and C(2′) were observed due to fast deuterium exchange.

Based on the facts presented above, we assigned the structure of 1-(1,2-dihydroxyethyl)-1-isopropylcyclononadecane (**1**) to the compound in question. We called it mediaglycol.

The mediaglycol molecule has a chiral carbon atom, C(1′). However, a solution of **1** (*c* 2.45) in a chloroform—methanol solvent mixture (3 : 1) showed a zero optical rotation when measured using a Polamat instrument. This fact can be explained by assuming that either compound **1** is a natural racemate or the magnitude of

Published in *Izvestiya Akademii Nauk, Seriya Khimicheskaya*, No. 11, pp. 1938—1940, November, 2000.

1066-5285/00/4911-1908 $25.00 © 2000 Kluwer Academic/Plenum Publishers

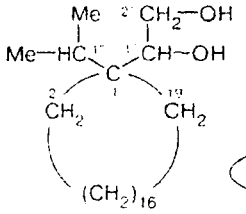
Table 1. Data of the NMR spectra of compound **1**

Atom	δ ^{13}C ($CDCl_3$)	δ ^1H (J/Hz)*	
		$CDCl_3$	CD_3OD
C(1)	29.80	—	—
C(2)**	33.28	1.15 (m)	1.23 (m)
C(3)–C(18)	29.70–29.96, 25.54, 27.42	1.24 (m)	1.39 (m)
C(19)**	39.09	1.43 (m)	1.53 (m)
C(1′)	72.34	3.44 (dd, J = 7.5, 10.9)	3.64 (m)
C(2′)	66.88	3.64 (m), 3.71 (m)	3.47 (dd, J = 6.6, 11.1); 3.56 (dd, J = 4.3, 11.1)
C(1″)	27.99	1.50 (septet, J = 6.6)	1.60 (septet, J = 6.6)
gem Me_2	22.65	0.85 (d, J = 6.6)	0.88 (d, J = 6.6)

* The integral intensities of the ^1H NMR signals correspond to the expected values.

** The signals of the corresponding ring methylene groups can be assigned alternatively.

the optical rotation is beyond the sensitivity of measurements.



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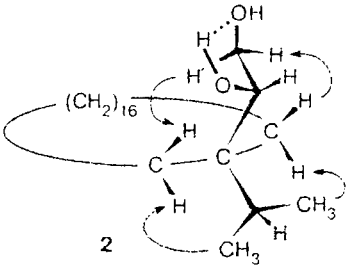

2

NOE

The 2D NOESY spectrum of compound **1** is deficient in cross-peaks. Only the interactions of the protons of the methyl and hydroxymethyl groups with different protons at the C(2) and C(19) ring atoms can be observed. This means that in a chloroform solution, the molecule has a conformation in which the side-chain protons are removed far from one another, as shown in formula **2**. In methanol, the intramolecular hydrogen bond in the α-glycol group is apparently cleaved and the side chain acquires a greater freedom of internal rotation, which is manifested in the ^1H NMR spectrum.

Natural products whose molecules contain saturated hydrocarbon macrocycles are very seldom encountered. Apart from the well-known muscone and civetone, only macrocyclic hydrocarbons isolated from the plant *Empetrum nigrum*,[9] are known.

Experimental

Melting points were determined using a Koffler hot stage. IR spectrum was recorded in a KBr pellet using a Bruker IFS 25 instrument. NMR spectra were run on a Bruker DRX-400 spectrometer in $CDCl_3$ and CD_3OD. The operation frequency was 400.13 MHz for ^1H and 100.62 MHz for ^{13}C. Mass spectrum (EI) was recorded on a Finnigan MAT 8200 instrument with direct injection (ionization energy 70 eV, ion source temperature 250 °C).

TLC was performed on Silufol plates in the $CHCl_3$–MeOH solvent system (95 : 5) using a 20% ethanol solution of phosphotungstic acid for visualization.

The above-ground parts of *Stellaria media* were gathered in the blooming period near Irkutsk (Eastern Siberia).

Isolation and purification of 1-(1,2-dihydroxyethyl)-1-isopropylcyclononadecane (mediaglycol) (1). Air-dried crushed plant material (2.2 kg) was extracted with hexane (20 L and 2×18 L) by infusion at ~20 °C. The combined extracts were concentrated *in vacuo* to dryness. The hexane extract (26 g) was separated into fractions by flash chromatography on silica gel (130 g, Lachema L 5/40 μm) using successively the $CHCl_3$–hexane (1 : 1, 500 mL) (*A*), $CHCl_3$ (700 mL) (*B*), and $CHCl_3$–MeOH (99 : 1, 200 mL; 97 : 3, 400 mL) (*C*) solvent systems as eluents. Elution with systems *A* and *B* resulted in the isolation of orange carotinoids, sterols, *etc.* Elution with mixture *C* (97 : 3) gave a fraction (0.3 g) containing compound **1** contaminated by fats and chlorophylls. Subsequent chromatography on silica gel (15 g, Lachema L 40/100 μm) in system *C* (99 : 1, 250 mL) afforded 70 mg of mediaglycol (**1**) (0.003%). Recrystallization from a $CHCl_3$–hexane mixture gave a colorless crystalline material (50 mg, 0.002%), m.p. 82–84 °C. Found (%): C, 78.12; H, 13.30. $C_{24}H_{48}O_2$. Calculated (%): C, 78.20; H, 13.12. MS, *m/z* (I_{rel} (%)): 368 $[M]^+$ (29.6), 340 (6.0), 153 (6.3), 139 (11.3), 127 (5.1), 125 (22.7), 113 (8.8), 111 (43.9), 99 (15.5), 97 (76.7), 85 (46.1), 83 (72.9), 71 (73.5), 69 (60.1), 57 (100.0), 55 (52.3), 43 (66.3), 29 (7.1). IR (KBr), ν/cm^{-1}: 3482 (OH); 3373 (OH); 2917, 2849, 1471, 1340, 719; 1384, 1368 (*gem* Me_2). The data of ^1H and ^{13}C NMR spectra are given in Table 1.

This work was supported by the Russian Foundation for Basic Research (Project No. 99-33-33012).

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Received December 14, 1999;
in revised form May 3, 2000