A simple improvement of the fit can be obtained by computing δ_{H_2O} from the following expression:

$$\delta_{H_2O} = \phi_2 \delta_{H_2O(2)} + \phi_3 \delta_{H_2O(3)} \quad (3)$$

where $\delta_{H_2O(2)}$ and $\delta_{H_2O(3)}$ refer to the values for δ_{H_2O} in the binary mixture. The fulldrawn curve in Fig. 2 has been computed from (1a) with δ_{H_2O} computed from (3). An excellent fit is obtained. By using (1b) instead of (1a) an equally good fit is obtained. For the sake of simplicity in computation (1a) is to be preferred.

Eqn. (3) implies that the interactions between water and a component in the mixture can be treated as if they are the same as in the pure solvent. This may be considered an indication that there are to a certain extent specific interactions between water and the two solvents. It is also possible that interactions between benzene and carbon tetrachloride partly are the reasons for the deviations. A 1:1 complex has been found to freeze out from this system [10] but this cannot be taken as a very strong argument in favor of its existence in solution. It is possible that an NMR study using water as a probe could elucidate on these points.

Acknowledgements. This work is part of a program financially supported by the *Swedish Natural Science Research Council* (NFR). Dr. Peter Staples corrected the English of the text.

1. Högfeldt, E. *Eleventh Scandinavian Chemist Meeting, Proc.*, p. 240, Åbo, Aug. 20–25, 1962.
2. Högfeldt, E. and Bolander, B. *Arkiv Kemi* **21** (1963) 161.
3. Ödberg, L. and Högfeldt, E. *Acta Chem. Scand.* **23** (1969) 1330.
4. Ödberg, L., Löfvenberg, A., Högfeldt, E. and Fredlund, F. *To be published.*
5. Högfeldt, *Thirteenth Scandinavian Chemist Meeting*, Copenhagen, Aug. 19–23, 1968.
6. Hildebrand, J. H. and Scott, R. L. *Solubility of Nonelectrolytes*, 3rd Ed., Reinhold, New York 1950, a, p. 266, b, p. 198.
7. Schatzberg, P. *J. Phys. Chem.* **67** (1963) 776.
8. Högfeldt, E. and Rasmuson, K. *Svensk Kem. Tidskr.* **78** (1966) 490.
9. Hildebrand, J. H. and Scott, R. L. *Regular Solutions*, Prentice-Hall, Englewood Cliffs, N.J. 1962, pp. 171–172.
10. Goates, J. R., Sullivan, R. J. and Ott, J. B. *J. Phys. Chem.* **63** (1959) 589.

Received June 10, 1970.

The Diterpenoids of *Solidago missouriensis* Nutt.

THORLEIF ANTHONSEN and GUDRUN BERGLAND

Institutt for organisk kjemi, Universitetet i Trondheim, Norges tekniske høgskole, Trondheim, Norway

In a series [1] of investigations of the genus *Solidago* we have isolated from an ethyl acetate extract of the roots of *Solidago missouriensis* Nutt. several diterpenoids (Table 1).

One of these, m.p. 90–92°, $[\alpha]_D^{24} = -26°$ ($CHCl_3$), has physical and spectroscopic [2,3] properties similar to 13-epi-*enantio*-manoyl-oxide (*1*), and a related, new, further oxygenated compound is on spectroscopic grounds proved to be 3-oxo-13-epi-*enantio*-manoyloxide (*2*) (m.p. 90–91°, $[\alpha]_D^{23} -53°$ ($CHCl_3$)), (IR 1705 cm^{-1}). Its mass spectrum is similar to the mass spectrum of 3-oxo-manoyloxide.[3]

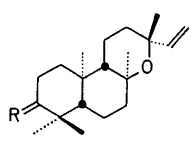
The strong peaks at *m/e* 206 and *m/e* 191 arising from the cleavage of bond C-9,C-11 and the C-8 oxide bond indicate that the keto group is in ring A or B.

The values obtained from the benzene-induced solvent shifts in the NMR spectrum of the ketone [4] then accord only with a 3-keto group. [τ(benzene)–$\tau(CDCl_3) = +0.25$ (C-10 Me), +0.03 (C-8 Me), +0.04 (C-13 Me), +0.08 (C-4 axial Me) and −0.17 ppm (C-4 equatorial Me)]. Neither a C-1, 2,[5] 6,[6] nor 7 keto function would produce a solvent shift in a methyl group of −0.17 ppm. A further indication of a 3-keto function is the two proton multiplet at τ 7.5 in the NMR spectrum.[2] The *enantio* stereochemistry at C-13 follows from the position of the three vinylic protons (τ_A 3.92, τ_B 5.00, τ_C 5.05, $J_{AB} = 18.0$, $J_{AC} = 10.5$, $J_{BC} = 1.3$ Hz).[2]

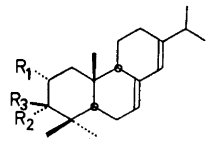
The remaining diterpenoids (*3*, *4*, *5*) all have one feature in common, a UV spectrum [λ_{max} (EtOH) 234, 241, 250 nm] diagnostic of a heteroannular diene system.[7] They all show olefinic signals in the NMR spectrum. One broad and one narrow multiplet around τ 4.5 (1 H C-7) and 4.2 (1 H C-14). This suggests that the compounds are 7,13-abietadienes. One of them, the ketone *3* (IR 1712 cm^{-1}), on Wolff-Kishner reduction furnishes a hydrocarbon shown by GLC to be identical with 7,13-abietadiene (*10*) produced from abietic

Table 1. Diterpenoids isolated from *Solidago missouriensis* Nutt. All compounds give satisfactory mass measurements.

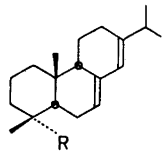
Compound No.	Name	Molecular formula	Methyl group resonances				
1	13-Epi-manoyloxide	$C_{20}H_{34}O$	8.82	9.13	8.96	9.19	9.28
2	3-Oxo-13-epi-monoyloxide	$C_{20}H_{32}O_2$	8.73	8.87	8.91	8.99	9.16
3	7,13-Abietadien-3-one	$C_{20}H_{30}O$	8.86	8.91	8.97	8.97(d)	
4	7,13-Abietadien-3β-ol	$C_{20}H_{32}O$	9.02	9.12	9.20	8.99(d)	
5	7,13-Abietadien-2α-ol acetate	$C_{22}H_{34}O_2$	8.93	9.04	9.10	8.96(d)	



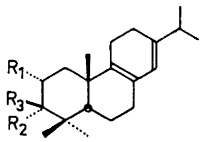
1 R=H_2
2 R=O



3 R_1=H, R_2, R_3=O
4 R_1=R_2=H, R_3=OH
5 R_1=OAc, R_2=R_3=H
11 R_1=OH, R_2=R_3=H



6 R=CO_2H
7 R=CO_2Me
8 R=CH_2OH
9 R=CHO
10 R=Me



12 R_1=H, R_2, R_3=O
13 R_1=R_2=H, R_3=OH
14 R_1=OAc, R_2=R_3=H

acid (*6*) by common reactions through the sequence *6* → *10*. LAH reduction of the ketone (*3*) gives an alcohol (*4*) which is identical with an alcohol occurring naturally in the plant. The NMR spectrum of this alcohol exhibits the carbinyl proton at τ 6.76 as a doublet of doublets (J=8.5 and 6.0 Hz) thus indicating an axial proton and in turn an equatorial hydroxy group. The remaining diterpenoid is an acetate (*5*) (IR 1740 cm^{-1}, NMR 7.97) which on hydrolysis gives an alcohol (*11*) different from the alcohol *4*. The alcohol *11* cannot be oxidized to a conjugated ketone.

The carbinyl proton of the acetate (*5*) appears at τ 5.11 in the NMR spectrum as a triplet of triplets. It is equally coupled to two neighbouring axial (J=12 Hz) and to two neighbouring equatorial protons (J=4 Hz), the size of the coupling constants revealing its axial nature and consequently the equatorial nature of the acetoxy group. On the basis of a 7,13-abietadiene skeleton only an acetoxy group at C-2 will have two neighbouring methylene groups.

We have good reasons to suppose that the 7,13-abietadienes (*3*, *4*, and *5*) are artefacts. The NMR spectra recorded immediately after the first purification did not contain the two olefinic signals at τ 4.2 and 4.5, but only one narrow signal at 4.5. This may be explained if the initial products obtained are 8,13-abietadienes (*12*, *13*, and *14*) which readily isomerize to the 7,13-abietadienes. This isomerization was also followed on TLC. Our studies in this problem will continue as soon as more plant material can be supplied.

Acknowledgements. One of us (G.B.) is grateful to the University of Trondheim, Norway Institute of Technology, for a fellowship. Curator Jan Tengner, Bergianska Trädgården, Stockholm, is thanked for providing the plants.

1. Anthonsen, T. and McCrindle, R. *Acta Chem. Scand.* **23** (1969) 1068.
2. Wenkert, E., Beak, P. and Grant, P.K. *Chem. Ind. (London)* **1961** 1574.
3. Enzell, C. R. and Ryhage, R. *Arkiv Kemi* **23** (1965) 367.
4. Connolly, J. D. and McCrindle, R. *Chem. Ind. (London)* **1965** 379.
5. Williams, D. H. and Bhacca, N. S. *Tetrahedron* **21** (1965) 2021.
6. Anthonsen, T., McCabe, P. H., McCrindle, R., Murray, R. D. H. and Young, G. H. R. *Tetrahedron* **26** (1970). *In press.*
7. Tabacik, C. and Poisson, C. *Bull. Soc. Chim. France* **1969** 3264.

Received June 8, 1970.