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Enumeration of isomers of acyclic saturated hydroxyl ethers

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In this paper, we present generating functions for counting constitutional isomers and stereo isomers of acyclic saturated compounds consisting of O, C and H for the first time, and obtain the numbers of constitutional isomers and stereo isomers of acyclic saturated hydroxyl ethers. The numerical results are tabulated.

KEY WORDS: enumeration, isomer, hydroxyl ether

Introduction

Besides hydrocarbons, acyclic saturated compounds consisting of O, C and H are the most important one class of all organic compounds. Acyclic saturated compounds consisting of O, C and H, include alcohols, ethers and hydroxyl ethers, and are especially valuable and useful among acyclic saturated organic compounds.

The enumerations of constitutional isomers, stereo isomers, chiral and achiral stereo isomers of alkanes have been reported [1–5]. The enumerations of isomers of alcohols ethers and some other compounds also have been reported [5–11], but the enumeration of isomers of individual hydroxyl ethers has not been seen. We present three generating functions for counting constitutional isomers, and stereo isomers of acyclic saturated compounds consisting of O, C and H, and obtain the numbers of constitutional isomers and stereo isomers of hydroxyl ethers with the graph-theoretical method.

1. Definitions

1.1. Stable C and O trees (alcohols, ether and hydroxyl ethers)

Consider a tree T, which consists of a finite set of two different kinds of points. One kind of points has degree 1–4, and is colored black, representing carbon atom; another kind of points has only degree 1 and 2, and is colored red. The number of each kind of points can be an arbitrary natural number. The tree is called a C and O tree.

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Stable C and O trees represent constitutional formulae for the acyclic saturated hydrocarbons, in which some oxygen atoms are inserted. Acyclic saturated compounds consisting of O, C and H can be alcohols, ethers or hydroxyl ethers. We simply call them “C and O compounds”. The “C and O compounds” have a characteristic, that is to say, in which each carbon atom can only adjoin to one oxygen atom, such as,

$CH_2(OH)CH(OH)CH_2OH$, $CH_3OCH_2CH_2OCH_2CH_3$ and $CH_3OCH_2CH_2OCH_2CH_2OH$.

But CH_3–O–CH_2OCH_3 and $(CH_3)_2C(OCH_3)_2$ are not considered, because hydrolysis of them gives aldehyde or ketone, being considered as derivatives of unsaturated compounds. Similarly, carboxylic acids, their esters, orthocarbonates, and orthoformates are not considered. Structures with per-oxo bonds also are not considered.

In this paper, each black point of degree 1–4 represents a carbon atom. Each red point of degree 1 or 2 represents an oxygen atom, hydrogen atoms being omitted. Each line joins two points.

1.2. *Planted C and O tree*

The acyclic saturated C and O compounds $C_iH_{2i+2}O_j$ can be constructed from alkyls (R) and alkoxyls (RO). The substituted alkyls can be classified into two kinds: the root carbon atom of an alkyl (R) can or cannot adjoin to an oxygen atom, the carbon atom that directly joins to an oxygen atom of an alkoxyl (RO) cannot adjoin to another oxygen atom. In order to simplify, in this paper, an alkyl is represented by R(I), an alkoxyl is represented by RO(II). A RO(II) removed the root oxygen atom, change as an alkyl R(II). Root carbon atom of alkyl R(II) cannot adjoins other oxygen atom any more.

A planted C and O tree is a C and O tree that besides the above-mentioned two kinds of points has a distinguishable point, which has degree 1–3, this point is called a root. A planted tree (I), in which the root point is a black point, represents a R(I). A planted tree (II), in which the root point is a black point, too, represents a R(II).

1.3. *Stereo C and O tree (including alcohols, ether and hydroxyl ethers)*

A stereo C and O tree with two different kinds of points is a C and O tree, in which four neighbors (neighboring points) of every carbon point are given a tetrahedral configuration. A stereo C and O tree with two different kinds of points represents a stereo formula of an acyclic saturated compound consisting of O, C and H.

1.4. *Planted stereo C and O tree*

Similarly, a planted stereo C and O tree with two different kinds of points is a stereo C and O tree, which also contains distinguishable root point besides the above-mentioned two kinds of points.

2. Counting

2.1. Constitution of alkyls R(I) and alkyls R(II)

Let $A(x, y)$ be the generating function of constitutional isomers of R(I) and $B(x, y)$ be the generating function of constitutional isomers of R(II). Then following standard Polya-theoretic techniques [3,4] coupled recursion relations for these generating functions may be developed. First recursion relation:

$$\begin{aligned} B(x, y) &= \sum_{i=0}^{\infty}\sum_{j=0}^{\infty} b_{ij}x^i y^j \\ &= 1 + y + \frac{1}{6}x\left[A^3(x, y) + 3A(x, y)A\left(x^2, y^2\right) + 2A\left(x^3, y^3\right)\right], \end{aligned} \tag{1}$$

where $b_{00} = 1$ and b_{ij} is the number of constitutional isomers of radical R(II) containing i carbon atoms and j oxygen atoms. Further $A(x, y)$ satisfies

$$\begin{aligned} A(x, y) &= \sum_{i=0}^{\infty}\sum_{j=0}^{\infty} a_{ij}x^i y^j \\ &= B(x, y) + \frac{1}{2}x\left[yB(x, y)A^2(x, y) + yB(x, y)A\left(x^2, y^2\right)\right], \end{aligned} \tag{2}$$

where a_{ij} is the number of constitutional isomers of R(I) containing i carbon atoms and j oxygen atoms.

2.2. Constitutional isomers of stable C and O tree and constitutional isomers of hydroxyl ethers

Let $C(x, y)$ be the generating function for counting *the stable C and O trees* with two different kinds of points, in which the coefficient c_{ij} of the term $x^i y^j$ is the number of constitutional isomers of acyclic saturated compounds consisting of O, C and H containing i carbon atoms and j oxygen atoms (i.e., c_{ij} is the total number of constitutional isomers of alcohols, ethers and hydroxyl ethers containing i carbon atoms and j oxygen atoms). Using the method of Harary et al. (see [4]), we can obtain the function and

$$\begin{aligned} C(x, y) &= \sum_{i=1}^{\infty}\sum_{j=0}^{\infty} c_{ij}x^i y^j \\ &= \frac{1}{24}x\left[A^4(x, y) + 4yB(x, y)A^3(x, y) + 6A^2(x, y)A\left(x^2, y^2\right)\right. \\ &\qquad + 12yB(x, y)A(x, y)A\left(x^2, y^2\right) + 3A^2\left(x^2, y^2\right) + 8A(x, y)A\left(x^3, y^3\right) \\ &\qquad \left. + 8yB(x, y)A\left(x^3, y^3\right) + 6A\left(x^4, y^4\right)\right] \\ &\quad - \frac{1}{2}\left[A(x, y) - 1\right]^2 + \frac{1}{2}\left[A\left(x^2, y^2\right) - 1\right] \\ &\quad - \frac{1}{2}y\left[B(x, y) - 1\right]^2 + \frac{1}{2}y\left[B\left(x^2, y^2\right) - 1\right]. \end{aligned} \tag{3}$$

Table 1
The numbers (c_{ij}) of constitutional isomers of acyclic saturated compounds consisting of C, O and H, $C_iH_{2i+2}O_j$.

$j\backslash i$	1	2	3	4	5	6	7	8	9	10	11	12
1	1	2	3	7	14	32	72	171	405	989	2426	6045
2	0	1	3	11	31	93	262	748	2094	5880	16392	45712
3	0	0	1	7	31	129	482	1715	5818	19217	61879	195861
4	0	0	0	2	14	92	478	2239	9503	37967	144110	526989
5	0	0	0	0	2	29	247	1652	9299	46739	215464	931358
6	0	0	0	0	0	4	61	673	5396	36051	209596	1102702
7	0	0	0	0	0	0	6	133	1759	16947	131384	874651
8	0	0	0	0	0	0	0	11	287	4601	51443	457639
9	0	0	0	0	0	0	0	0	18	635	11812	152289
10	0	0	0	0	0	0	0	0	0	37	1408	30249
11	0	0	0	0	0	0	0	0	0	0	66	3158
12	0	0	0	0	0	0	0	0	0	0	0	135

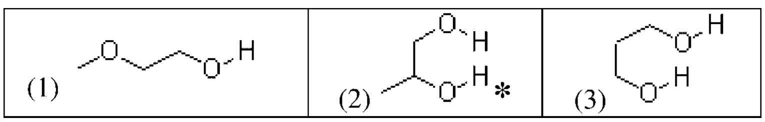

Figure 1. Three constitutional isomers ($i = 3$, $j = 2$) in table 1.

The numerical results are given in table 1.

Let $C1(x, y)$ be the generating function for counting constitutional isomers of the acyclic saturated alcohols (for the numerical results, see [7, table 1]). Let $C2(x, y)$ be the generating function for counting constitutional isomers of the acyclic saturated ethers (for the numerical results, see [8, table 1]). Let $C3(x, y)$ be the generating function for counting constitutional isomers of the acyclic saturated hydroxyl ethers.

In addition, $C(x, y)$ is the generating function for counting the stable C and O trees that represents constitutional isomers for alcohols, ether and hydroxyl ethers, i.e.,

$$C(x, y) = C1(x, y) + C2(x, y) + C3(x, y). \tag{4}$$

Then, we can obtain

$$C3(x, y) = C(x, y) - C1(x, y) - C2(x, y). \tag{4'}$$

The numerical results are given in table 2.

For example, when $i = 3$ and $j = 2$, $c_{32} = 3$, the corresponding three constitutional isomers are given in figure 1. The structure with "$*$" has two stereo realizations. The structure (1) is a hydroxyl ether.

When $i = 4$ and $j = 2$, $c_{42} = 11$, the eleven constitutional isomers are given in following figure 2. The structure with "$**$" has three stereo realizations.

In figure 2, there are 4 structures, (8)–(11), that belong to hydroxyl ethers ($c3_{42} = 4$, table 2).

Table 2
The numbers ($c3_{ij}$) of constitutional isomers of hydroxyl ethers.

$j\backslash i$	1	2	3	4	5	6	7	8	9	10	11	12
1	0	0	0	0	0	0	0	0	0	0	0	0
2	0	0	1	4	14	43	128	369	1051	2962	8305	23188
3	0	0	0	3	17	82	326	1209	4202	14092	45849	146131
4	0	0	0	0	6	55	335	1692	7532	30973	119956	444716
5	0	0	0	0	0	14	159	1230	7445	39147	185787	819436
6	0	0	0	0	0	0	29	440	4166	29898	181487	981606
7	0	0	0	0	0	0	0	67	1219	13464	111825	775286
8	0	0	0	0	0	0	0	0	145	3260	41726	396947
9	0	0	0	0	0	0	0	0	0	329	8538	125598
10	0	0	0	0	0	0	0	0	0	0	736	22179
11	0	0	0	0	0	0	0	0	0	0	0	1675
12	0	0	0	0	0	0	0	0	0	0	0	0

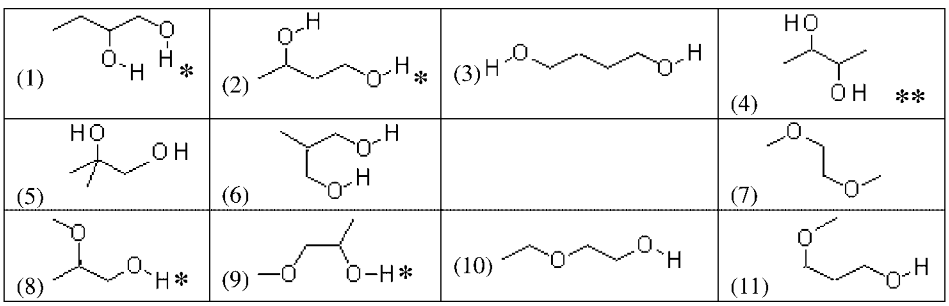

Figure 2. Eleven structures ($i = 3$, $j = 2$) in table 1.

2.3. *Stereo isomers of alkyls R(I) and alkyls R(II)*

Let $D(x, y)$ be the generating function for stereo isomers of R(I) and $E(x, y)$ be the generating function of stereo isomers of R(II). Then they obey the following coupled recursion relations, basing on the method of Robinson et al. [6]:

$$E(x, y) = \sum_{i=0}^{\infty} \sum_{j=0}^{\infty} e_{ij} x^i y^j = 1 + \frac{1}{3} x \left[D^3(x, y) + 2D\left(x^3, y^3\right) \right], \tag{5}$$

$$D(x, y) = \sum_{i=0}^{\infty} \sum_{j=0}^{\infty} d_{ij} x^i y^j = E(x, y) + xyE(x, y) D^2(x, y), \tag{6}$$

where the $d_{00} = 1$ and e_{ij} is the number of stereo isomers of RO(II) containing i carbon atoms and j oxygen atoms; d_{ij} is the number of stereo isomers of R(I) containing i carbon atoms and j oxygen atoms.

Table 3
The numbers (f_{ij}) of stereo isomers of acyclic saturated compounds consisting of C, O and H, $C_iH_{2i+2}O_j$.

$j\backslash i$	1	2	3	4	5	6	7	8	9	10	11	12
1	1	2	3	8	18	47	123	338	935	2657	7616	22138
2	0	1	4	17	57	194	640	2104	6854	22280	72198	233697
3	0	0	1	12	70	355	1579	6578	26044	99939	373818	1373165
4	0	0	0	4	38	318	2039	11339	56793	265119	1173410	4990262
5	0	0	0	0	6	123	1334	10832	72776	431239	2330909	11766074
6	0	0	0	0	0	19	422	5666	54936	435165	2984044	18412157
7	0	0	0	0	0	0	49	1465	23474	268393	2457138	19229527
8	0	0	0	0	0	0	0	150	5170	96981	1275238	13293554
9	0	0	0	0	0	0	0	0	442	18458	396733	5927014
10	0	0	0	0	0	0	0	0	0	1424	66508	1616496
11	0	0	0	0	0	0	0	0	0	0	4522	241376
12	0	0	0	0	0	0	0	0	0	0	0	14924

2.4. *Stereo isomers of C and O compounds and hydroxyl ethers*

Similarly, let $F(x, y)$ be the generating function for stereo isomers of acyclic saturated compounds consisting of O, C and H. We can get

$$\begin{aligned} F(x, y) &= \sum_{i=1}^{\infty}\sum_{j=0}^{\infty} f_{ij}x^i y^j \\ &= \frac{1}{12}x\big[D^4(x, y) + 4yE(x, y)D^3(x, y) + 3D^2\big(x^2, y^2\big) + 8D(x, y)D\big(x^3, y^3\big) \\ &\qquad + 8yE(x, y)D\big(x^3, y^3\big)\big] - \frac{1}{2}\big[D(x, y) - 1\big]^2 + \frac{1}{2}\big[D\big(x^2, y^2\big) - 1\big] \\ &\quad - \frac{1}{2}y\big[E(x, y) - 1\big]^2 + \frac{1}{2}y\big[E\big(x^2, y^2\big) - 1\big], \end{aligned} \tag{7}$$

where f_{ij} is the number of numbers of stereo isomers of acyclic saturated compounds consisting of C, O and H, $C_iH_{2i+2}O_j$ containing i carbon atoms and j oxygen atoms. Some results are given in table 3.

Let $F1(x, y)$ be the generating function for counting constitutional isomers of the acyclic saturated alcohols (for the numerical results, see [7, table 2]). Let $F2(x, y)$ be the generating function for counting constitutional isomers of the acyclic saturated ethers (for the numerical results, see [8, table 2]). Let $F3(x, y)$ be the generating function for counting constitutional isomers of the acyclic saturated hydroxyl ethers being similar to $C3(x, y)$,

$$F3(x, y) = F(x, y) - F1(x, y) - F2(x, y). \tag{8}$$

Some results are given in table 4.

In table 4, when $i = 4$ and $j = 2$, $f3_{42} = 6$, the corresponding six structures are given in figure 3.

Table 4
The numbers ($f3_{ij}$) of stereo isomers of hydroxyl ethers.

$j\backslash i$	1	2	3	4	5	6	7	8	9	10	11	12
1	0	0	0	0	0	0	0	0	0	0	0	0
2	0	0	1	6	24	86	296	992	3276	10732	34979	113650
3	0	0	0	4	34	205	982	4290	17494	68478	259810	964432
4	0	0	0	0	13	166	1277	7808	41391	200462	910263	3943526
5	0	0	0	0	0	46	742	7192	53072	333136	1870460	9697422
6	0	0	0	0	0	0	159	3267	37860	329678	2394312	15341848
7	0	0	0	0	0	0	0	579	13974	190489	1915164	15859497
8	0	0	0	0	0	0	0	0	2076	59067	925575	10587859
9	0	0	0	0	0	0	0	0	0	7582	246385	4380875
10	0	0	0	0	0	0	0	0	0	0	27730	1019722
11	0	0	0	0	0	0	0	0	0	0	0	102116
12	0	0	0	0	0	0	0	0	0	0	0	0

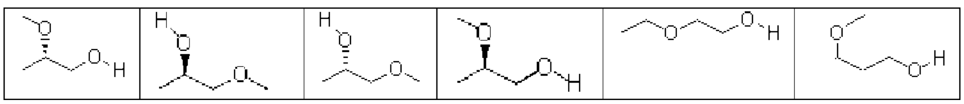

Figure 3. When $i = 4$ and $j = 2$, six stereo isomers ($f3_{42} = 6$) of the compounds, $C_4H_{10}O_2$, belonging to hydroxyl ethers.

2.5. *Achiral stereo isomers of C and O compounds and hydroxyl ethers*

Let $G(x, y)$ be the generating function of achiral stereo isomers of R(I) and $H(x, y)$ be the generating function of achiral stereo isomers of R(II). Then, they obey the following coupled recursion relations:

$$H(x, y) = \sum_{i=0}^{\infty}\sum_{j=0}^{\infty} g_{ij}x^i y^j = 1 + xG(x, y)D\big(x^2, y^2\big), \tag{9}$$

where the $g_{00} = 1$ and h_{ij} is the number of achiral stereo isomers of R(II) containing i carbon atoms and j oxygen atoms;

$$G(x, y) = \sum_{i=0}^{\infty}\sum_{j=0}^{\infty} g_{ij}x^i y^j = H(x, y) + xyH(x, y)D\big(x^2, y^2\big), \tag{10}$$

where g_{ij} is the number of achiral stereo isomers of R(I) containing i carbon atoms and j oxygen atoms. Let $L(x, y)$ be the generating function of achiral stereo isomers of acyclic saturated compounds consisting of O, C and H. We can get

$$\begin{aligned} L(x, y) &= \sum_{i=1}^{\infty}\sum_{j=0}^{\infty} l_{ij}x^i y^j \\ &= \frac{1}{2}xD\big(x^4, y^4\big) + \frac{1}{2}xG^2(x, y)D\big(x^2, y^2\big) + xyH(x, y)G(x, y)D\big(x^2, y^2\big) \end{aligned}$$

Table 5
The numbers (l_{ij}) of achiral stereo isomers of acyclic saturated compounds consisting of C, O and H, $C_iH_{2i+2}O_j$.

$j\backslash i$	1	2	3	4	5	6	7	8	9	10	11	12
1	1	2	3	6	10	19	33	62	109	203	360	666
2	0	1	2	7	13	34	62	144	262	572	1040	2185
3	0	0	1	4	12	35	83	206	450	1025	2146	4647
4	0	0	0	2	6	28	67	227	509	1427	3058	7748
5	0	0	0	0	2	11	44	160	470	1397	3601	9520
6	0	0	0	0	0	5	16	106	294	1211	3090	10169
7	0	0	0	0	0	0	5	33	160	677	2320	7883
8	0	0	0	0	0	0	0	14	50	397	1218	5874
9	0	0	0	0	0	0	0	0	14	102	581	2758
10	0	0	0	0	0	0	0	0	0	42	156	1488
11	0	0	0	0	0	0	0	0	0	0	42	330
12	0	0	0	0	0	0	0	0	0	0	0	132

Table 6
The numbers ($l3_{ij}$) of achiral stereo isomers of hydroxyl ethers.

$j\backslash i$	1	2	3	4	5	6	7	8	9	10	11	12
1	0	0	0	0	0	0	0	0	0	0	0	0
2	0	0	1	2	6	12	26	50	100	188	365	680
3	0	0	0	2	6	21	50	130	282	650	1346	2914
4	0	0	0	0	3	14	47	150	383	1026	2355	5726
5	0	0	0	0	0	6	24	114	338	1102	2856	7864
6	0	0	0	0	0	0	9	55	216	862	2526	8152
7	0	0	0	0	0	0	0	19	90	501	1730	6497
8	0	0	0	0	0	0	0	0	28	209	917	4279
9	0	0	0	0	0	0	0	0	0	60	333	2091
10	0	0	0	0	0	0	0	0	0	0	90	788
11	0	0	0	0	0	0	0	0	0	0	0	198
12	0	0	0	0	0	0	0	0	0	0	0	0

$$
\begin{aligned}
&-\frac{1}{2}\big[G(x,y)-1\big]^2+\frac{1}{2}\big[D\big(x^2,y^2\big)-1\big] \\
&-\frac{1}{2}y\big[H(x,y)-1\big]^2+\frac{1}{2}y\big[E\big(x^2,y^2\big)-1\big],
\end{aligned}
\tag{11}
$$

where l_{ij} is the number of numbers of achiral stereo isomers of acyclic saturated compounds consisting of C, O and H, $C_iH_{2i+2}O_j$ containing i carbon atoms and j oxygen atoms.

Let $L1(x,y)$ be the generating function for counting constitutional isomers of the acyclic saturated alcohols (for the numerical results, see [7, table 3]). Let $L2(x,y)$ be the generating function for counting constitutional isomers of the acyclic saturated ethers (for the numerical results, see [8, table 3]). Let $L3(x,y)$ be the generating function for counting constitutional isomers of the acyclic saturated hydroxyl ethers. Being similar to $C3(x, y)$,

$$L3(x, y) = L(x, y) - L1(x, y) - L2(x, y). \tag{12}$$

Some numerical results are given in tables 5 and 6.

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