The presence of numerous complex organic molecules (COMs; defined as those containing six or more atoms) around protostars shows that star formation is accompanied by an increase of molecular complexity. These COMs may be part of the material from which planetesimals and, ultimately, planets formed. Comets represent some of the oldest and most primitive material in the solar system, including ices, and are thus our best window into the volatile composition of the solar protoplanetary disk. Molecules identified to be present in cometary ices include water, simple hydrocarbons, oxygen, sulfur, and nitrogen-bearing species, as well as a few COMs, such as ethylene glycol and glycine. We report the detection of 21 molecules in comet C/2014 Q2 (Lovejoy), including the first identification of ethyl alcohol (ethanol, C₂H₅OH) and the simplest monosaccharide sugar glycolaldehyde (CH₂OHCHO) in a comet. The abundances of ethanol and glycolaldehyde, respectively 5 and 0.8% relative to methanol (0.12 and 0.02% relative to water), are somewhat higher than the values measured in solar-type protostars. Overall, the high abundance of COMs in cometary ices supports the formation through grain-surface reactions in the solar system protoplanetary disk.

RESULTS

In the spectral survey of comet Lovejoy, we detected lines of 21 molecules (Table 1), two of which, ethyl alcohol (ethanol, C₂H₅OH) and glycolaldehyde (CH₂OHCHO), were detected for the first time in a comet. We secured the detection of ethanol and glycolaldehyde by averaging the strongest lines present in the observed spectral domain. Ethanol is detected through lines of both trans and gauche conformers. Most other detected COMs and simple organic molecules, such as ethylene glycol [(CH₂OH)₂], methyl formate (HCOOCH₃), formamide (NH₂CHO), formic acid (HCOOH), and acetaldehyde (CH₃CHO), were first detected in comet Hale-Bopp and later confirmed in other comets (6–8). Figure 1 shows the spectra of eight organic species detected in comet Lovejoy.

Relative abundances can be estimated by deriving molecular production rates from the observed line intensities. In this active comet, most molecules within the field of view are close to local thermal equilibrium (LTE). To take into account departures from LTE in the less dense parts of the coma due to radiative decay, the line intensities were analyzed using an excitation model (11, 12). From the numerous detected methanol lines, we derived a rotational temperature of 680 ± 0.7 K and a gas temperature of 73 K. Assuming isotropic outgassing, and using the gas velocity of 0.8 km/s derived from the spectrally resolved strong lines, we determined the production rate for all observed molecules (1). Table 1 provides the abundances relative to water, using water production rates of Q_H₂O = 5 × 10⁻⁹ and 6 × 10⁻⁹ molecules s⁻¹ for the periods 13–16 and 23–26 January 2015, respectively. These values were deduced from the observations of the OH radical and H₂O performed with the Nançay radio telescope and Odin space observatory, respectively, in January 2015. The conformers of ethanol were found to be in the relative proportion trans/gauche of 1.5 ± 0.3. Because of the low energy barrier between the two ethanol conformers (~57 K), trans-to-gauche interconversion was rapid in the collisional region of the comet (less than 1 ps at 73 K), whereas interconversion through radiative decay was expected to be slow (13). The trans/gauche ratio was close to the equilibrium value of 1.1 expected at the temperature of the sampled gas (73 K).
DISCUSSION

Production rates relative to water measured in comet Lovejoy are lower by a factor of 2 to 3 than those in comet Hale-Bopp, except for CH$_3$OH and HCOOCH$_3$, which show similar abundances, and for cyanoacetylene (HC$_3$N), which is depleted in Lovejoy by a factor of 10 (6). Another notable exception is CO, which is a factor of >10 less abundant in Lovejoy, but Hale-Bopp belongs to the small family of CO-rich comets (14). The depletion remains when comparing with abundances measured in comets other than Hale-Bopp (table S2). Composition diversity is often observed in the comet population, but this is the first time that depletion is observed for such a large number of molecules in a comet.

Ethanol and glycolaldehyde, as well as the other COMs observed in comets, are found in warm (≥100 K) regions surrounding newly born stars, at the time when the collapsing envelope feeding the star has not yet dissipated (2). These regions, called hot corinos or cores for low- or high-mass protostars, exhibit a rich molecular inventory dominated by saturated species. COMs may have been synthesized in the cold prestellar core period by grain-surface reactions, when all heavy element-bearing molecules were frozen onto grains (15, 16). The efficiency of surface chemistry is increased during the warm-up phase because of the increased mobility of atoms and radicals on warm grains, producing large molecules (17). It is not clear to what extent these compounds are preserved in the protoplanetary disk. However, chemical models show that COMs are also efficiently formed on grain surfaces in the disk owing to the intense UV illumination from the newly born star (17). The presence of interstellar-like organic compounds in comets suggests that they are preserved materials synthesized in the outskirts of the solar nebula or at earlier stages of solar system formation.

In Fig. 2, the abundances (normalized to methanol) of nine organic molecules measured in comets Lovejoy and Hale-Bopp are compared to those measured in two interstellar sources. Orion-KL is the best-studied hot-core source because of its proximity and molecular wealth. Quantitative comparison with comets is restricted to methanol, ethanol (C$_2$H$_5$OH), ethylene glycol [(CH$_2$OH)$_2$], and glycolaldehyde (CH$_2$OHCHO) measured at the same position in Orion-KL (18). The ethylene glycol abundance in this source is much lower than those in the four comets, where it has been detected, and this conclusion also applies to the hot-core Sgr B2(N) (8, 18). Glycolaldehyde has not been detected in Orion-KL (18), but the derived abundance upper limit (not shown in the figure) is also much lower than the value measured in comet Lovejoy. IRAS 162293-2422 is the best-studied hot corino. The two components of this solar-type binary protostar exhibit large compositional differences, with sources A and B being richer in nitrogen- and oxygen-bearing molecules, respectively (10). There is an overall agreement between source B and comet organic composition (Fig. 2), although comets are much richer in ethylene glycol (by two orders of magnitude) and ethanol (by a factor of 6), whereas they are depleted in ketene (CH$_2$CO). Contrarily to Orion-KL, IRAS 162293-2422(B) (19) is moderately underabundant (by a factor of 2.5) in glycolaldehyde compared to comet Lovejoy. The same properties are observed for other hot corinos (20).

Comparison with protoplanetary disks is more difficult. The molecules observed in protoplanetary disks are mainly small species and associated isotopologs. The most complex identified species are H$_2$CO, HC$_3$N, CH$_3$CN, and C$_2$H$_2$ (21–24). The HCN/HC$_3$N/CH$_3$CN abundances are estimated to be in the 1:0.05–0.2:0.05–0.2 proportion in the MCW 480 disk, at radial distances corresponding to the comet formation zone (24). This compares well with ratios measured in comets, for example, 1:0.02:0.16 and 1:0.08:0.08 in comets Lovejoy and Hale-Bopp, respectively. A comparison with COM abundances in protoplanetary disks expected from chemical models (25) is shown in Fig. 2. In addition to grain-surface reactions, reactive desorption and irradiation of ice mantle material in the mid-plane of the disk are included in the chemical model, and enhance the abundances of the more complex molecules in the disk grains (25). However, ethylene glycol is produced with a negligible abundance in this model, which implies that efficient formation routes must be found to explain its large abundance in comets (25). Whereas ethylene glycol formation is investigated through the addition of two CH$_2$OH radicals (25), an alternative grain-surface formation route in protoplanetary disks involves sequential atom-atom additions (26), for which reaction rates and reaction barriers need to be measured.
for implementation in chemical models. Altogether, the high COM abundances in cometary ices, often higher than the hot-corino abundances (Fig. 2), are in line with their synthesis through grain-surface reactions and ice irradiation in the early solar nebula.

Although the possible role of comets in the delivery of terrestrial water has recently been questioned in favor of an asteroidal source (27), the COMs found in comets, which have their origin in the volatile phase of the solar nebula, are likely related to those present in asteroids (28). The identification of biologically important COMs in cometary ices is thus an important step toward our understanding of the origin of life on Earth.

Fig. 1. Spectra of organics in comet C/2014 Q2 (Lovejoy). The observations were obtained with the IRAM 30m radio telescope in the 211–272 GHz band between 13 and 25 January 2015. The velocity scale is in the nucleus rest frame. Intensity is given in the main beam temperature scale. Spectra, from top left, are glycolaldehyde (CH2OHCHO, average of two lines), ethyl alcohol (ethanol, C2H5OH, average of 13 lines), aG' ethylene glycol [(CH2OH)2, average of 14 lines], methyl formate (HCOOCH3, average of two groups of blends of several lines, whose positions are marked by blue arrows), formic acid (HCOOH, average of six lines), acetaldehyde (CH3CHO, average of 40 lines), isocyanic acid [HNCO(110,11–100,10) at 241.774 GHz], and formamide (NH2CHO, average of 10 lines). The signal-to-noise ratio is 6 for glycolaldehyde, 10 for ethanol, and higher than 7 for the other molecules.

Fig. 2. Abundances of complex organics in comets and protostars. The abundances measured in comets Lovejoy (Table 1) and Hale-Bopp (Table S2) are compared with those measured in the low-mass protostar IRAS 16293-2422(B) (19, 33) and in the high-mass protostar Orion-KL (18) and with results from chemical modeling in a protoplanetary disk (25). Abundances are given relative to CH3OH, the most abundant organic molecule in these sources. H2CO values may be less relevant because, for comets, a significant fraction is released from grains (34), whereas for IRAS 16293-2422, the plotted value pertains to the sum of the contributions to the two components A and B of the binary source. For CH3CO, the black triangle is a 3σ upper limit obtained in comet Lovejoy.

MATERIALS AND METHODS

Observations
Comet C/2014 Q2 (Lovejoy) was observed with the IRAM 30m radio telescope during two periods: on 13.8, 15.8, and 16.8 January 2015 (geocentric distance ∆ = 0.496 to 0.528 AU) and on 23.7, 24.7, 25.7, and 26.7 January 2015 (∆ = 0.624 to 0.675 AU) with very good weather conditions. Perihelion was on 30.07 January UT, at 1.290 AU from the Sun. The 13–25 and 26 January observations were obtained with the EMIR 1- and 3-mm receivers, respectively. The main backend we used was a Fourier transform spectrometer, which covers a frequency range of 2 × 8 GHz (two side bands separated by 8 GHz, each in two linear polarizations) in a single setup, with a high spectral resolution of 200 kHz. The spectral resolution (0.3 to 0.2 km s⁻¹ when converted into Doppler velocity) allows the determination of the velocity profile of the narrow cometary lines (~2 km s⁻¹). Using three different tunings, we covered the 210–25 and 26 January observations were obtained with the EMIR 1- and 3-mm receivers, respectively. The main backend we used was a Fourier transform spectrometer, which covers a frequency range of 2 × 8 GHz (two side bands separated by 8 GHz, each in two linear polarizations) in a single setup, with a high spectral resolution of 200 kHz. The spectral resolution (0.3 to 0.2 km s⁻¹ when converted into Doppler velocity) allows the determination of the velocity profile of the narrow cometary lines (~2 km s⁻¹). Using three different tunings, we covered the 210–218, 225–233, and 240–272 GHz frequency ranges. Given the excitation conditions encountered in cometary coma at 1 to 1.5 AU from the Sun, most of the molecules have their strongest lines in this frequency domain. Complex cometary molecules have many lines expected to have similar intensities in this domain, and we obtained secure detections when averaging the signal of the lines expected to be the strongest according to our models (8). The number of lines detected with a signal-to-noise ratio higher than 3 was respectively 2 for CH3OHCHO, 8 for C2H5OH, 2 for HCOOCH3, 37 for CH3CHO, 7 for (CH2OH)2, 9 for HCOOH, 10 for NH2CHO, and 4 for HNCO. Seven lines were used for the upper limit on ketene (CH3CO).
The half-power beamwidth of IRAM 30m at these frequencies ranged from 9.1” to 11.6”, which corresponded to 3300 to 5400 km at the comet distance. The pointing accuracy, which was regularly checked on reference pointing sources and also on the comet with coarse maps of the strongest lines, was better than 2”.

The time variation of the activity of the comet could be monitored because of the presence of several strong CH₃OH lines in each setup. We did not see any variation greater than ±20% during the observations [Q₆CH₃OH = 1.2 ± 0.2 × 10²⁸ molecules s⁻¹ (13–16 January) and 1.4 ± 0.2 × 10²⁸ molecules s⁻¹ (23–25 January)]. This justifies the averaging of several days of observations to improve the signal-to-noise ratio and to derive production rates that are more precise. Table S1 provides a list of the strongest ethanol and glycolaldehyde lines identified in the spectra and the production rates derived for each line. Several other lines are individually present only at the 1σ to 3σ level but yield a detection when combined together and were used to compute production rates.

Excitation models and production rate determination

For all molecules, we used the latest spectroscopic data available in the JPL (29) or CDMS (30) database, both for line identification and computation of line strengths. In our model, the population distribution of the ground vibrational state of molecule slowly evolves with the computation of line strengths. In our model, the population distribution of the ground vibrational state of molecule slowly evolves with the computation of line strengths.

For ketene, we obtain a marginal 3σ value of 4.3 ± 1.4 × 10²⁵ molecules s⁻¹ (0.008% relative to water), but the detection of this molecule needs to be confirmed in a brighter comet. Ethanol is expected to be either in the trans or gauche states, which are treated separately in our model. Trans and gauche lines yield similar production rates for both conformers (Q₉trans = 4.6 ± 0.6 × 10²⁶ molecules s⁻¹, Q₉gauche = 3.0 ± 0.4 × 10²⁶ molecules s⁻¹). The measured ethanol trans/gauche ratio of 1.5 ± 0.3 (1.0 ± 0.2 if we take only the 14 lines with signal-to-noise ratio ≥2 from table S1) corresponds to a conformeric equilibrium temperature of 51 ± 11, K, slightly lower but close to the Tgas derived above. Using a cooler temperature for ethanol will not significantly change the derived abundance. The intensity and derived total production rates for the strongest lines of glycolaldehyde and ethanol (assuming 50% in each state for ethanol) are provided in table S1. In the case of the NS radical, we have computed the production rate and abundance, assuming a release from close to the nucleus.

Water production rate

The reference water production rate was primarily derived from observations of the OH radical maser lines at 18 cm carried out with the Nançay radio telescope at the same time. During the 12–17 January period, observations centered on the comet and at 3.0’’ offset positions (fig. S3) were used to constrain the quenching of the maser inversion (32) yielding an average water production rate QH₂O = 5.0 ± 0.2 × 10²⁹ molecules s⁻¹. OH observations performed between 18 and 25 January were all centered on the nucleus so the water production rates are less constrained for this period. Observations of H₂O were performed with the Odin satellite on 30 January to 3 February (fig. S3). Analysis of both centered and offset positions up to 3’’ yields an average production rate QH₂O = 7.5 ± 0.3 × 10²⁹ molecules s⁻¹. Because several methanol lines were detected in each observing setup with the IRAM 30m, we also used the methanol production rate as a proxy for the evolution of water outgassing, correcting possible biases due to larger pointing uncertainties during the period 23–25 January (no coarse mapping was available). From the interpolation of the Nançay and Odin measurements, we estimate that during the period of 23–25 January, QH₂O ≈ 6.0 × 10²⁹ molecules s⁻¹. The uncertainty on the water outgassing rate should be less than 10%, but we cannot fully exclude that part of the water vapor observed in the 2’’ to 8’’ Odin and Nançay beams comes from the sublimation of icy grains conducting to an overestimate of the water outgassing from the nucleus surface. Nevertheless, we do not find clear evidence for a distributed source of gases in the coma of comet Lovejoy: coarse maps of HCN and CH₃OH up to 20’’ from the nucleus show no evidence for a distributed source, and the interpretation of the Odin water maps does not require considering a distributed source of H₂O beyond 1’’.

SUPPLEMENTARY MATERIALS

Supplementary material for this article is available at http://advances.sciencemag.org/cgi/content/full/1/6/e1500863/DC1

Table S1. Observed strongest lines and production rates.
Table S2. Abundances relative to water.
Fig. S1. Rotational diagram of the methanol lines observed between 248 and 256 GHz.
Fig. S2. Rotational diagram of the methanol lines observed around 242 GHz.
Fig. S3. Water production rate: OH and H₂O observations.
Ethyl alcohol and sugar in comet C/2014 Q2 (Lovejoy)
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